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REFERENCE

Lane, B. H., 1935, Suggestions to authors of papers submitted for publication by the United States Geological Survey: U. S. Geol. Survey, Washington, D. C. (For sale by Superintendent of Documents, Washington, D. C. 25c.)

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American Journal of Science

APRIL 1956

THE SERPENTINITE MASS IN GLEN URQUHART, INVERNESS-SHIRE, SCOTLAND

G. H. FRANCIS

ABSTRACT. An account is given of the field occurrence and mineralogy of an ultrabasic intrusive mass in the Highlands of Scotland. Attention is given to the optical characters of the serpentine minerals in the light of recent X-ray and electron microscope work. The chemistry of the mass is compared with that of similar ultrabasic masses thought to be derived from the peridotite shell of the Earth. Evidence suggesting solid intrusion is given and the nature of the serpentinization process is discussed. The petrography of mesh serpentinite is described, as is its alteration to antigorite. The effects of metasomatic fluids of older granite (synorogenic, postkinematic) on the already serpentinized mass are described, and a chemical analysis illustrates an early phase of this alteration.

INTRODUCTION

The serpentine mass in Glen Urquhart is a pod-shaped body 0.89 square mile in area. It is mentioned in a paragraph of the Geological Survey of Scotland Memoir for sheet 93 by E. H. Cunningham Craig (1914, p. 23). The present study confirms all Cunningham Craig's findings. The mass intruded already folded and metamorphosed sediments of the Moine Series. These consist of psammitic schist with amphibolite sills and lenticles, kyanite-garnet schist, and impure marble. They will be described elsewhere. After periods of intrusion and serpentinization of the ultrabasic a period of injection metasomatism affected the mass and the surrounding sediments. This is correlated with the widespread injection of the Older Granite of the Highlands.

FIELD OCCURRENCE

The serpentinite is unmistakable in the field, supporting less vegetation than its surrounding sediments. Everywhere bare *roches moutonées* of serpentinite stand out from the heather. They weather buff, and are deeply seamed and furrowed following foliation planes in the rock. The commonest rock type occurs along the center of the intrusion. Beneath the buff weathering crust is a dull black ground set with lustrous black rectangular bodies. These are "bastite" pseudomorphs. They lie haphazardly, measuring 2. cm x 0.3 cm approximately, though with some variation in the size of the prisms. Near the margins of the mass the "bastite" rock often gives place to a rock on whose weathered surfaces rounded marks, like worm-casts, stand proud. These are gray-white pods composed of tremolite or tremolite and chlorite often sheathed in iron ores. Net veining is often prominent in these marginal rocks. Occasionally they are much sheared and resemble rough slates. Lastly there are small patches of massive or brittle jade-green rocks. Under the microscope these are seen to be examples of the replacement of mesh serpentine by antigorite.

The injection metasomatism is evinced by small irregular bodies at or near the serpentinite margin. Their parageneses are similar to those of marginal zones of serpentinites from many areas (e.g. F. C. Phillips, 1927; Hess, 1933a, 1933b; Read, 1933; A. H. Phillips and Hess, 1936; Amin, 1952). Typical minerals are actinolite, anthophyllite, chlorite, talc, and magnesite. These are not in continuous zones as are others, described by the above authors. They are small and scattered bodies, not always right at the contacts of the mass. An incipient alteration to be grouped with these rocks is the formation of the chlorite-tremolite-ore pods; another is the increase of talc towards the contacts.

The marginal bodies are inconspicuous in the field, weathering to the same buff color as the serpentinite. Very rough surfaces are often found on coarse amphibole or chlorite aggregates. There are occasional pale rocks, with sheafs of light green talc pseudomorphous after anthophyllite, a feature typical of many New England ultrabasics (J. B. Thompson, personal communication). Bottle-green prisms of actinolite occur, set in a pale ground of chlorite, talc and magnesite stained with iron oxide.

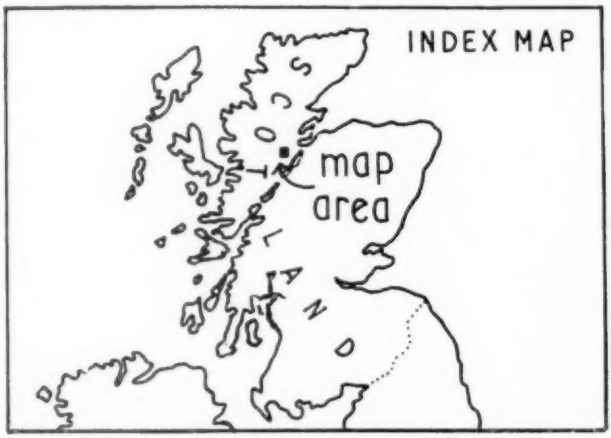


Fig. 1-A. Index map.

STRUCTURE

A clear intrusive relationship can be seen between the serpentinite mass and its surrounding sediments. They do not, however, show any recognizable contact metamorphism. It is also clear that the intrusion postdated the acme of folding and metamorphism of the sediments. On the east side of the mass its margin truncates folds in the wall rock. At the north end of the mass it holds a block of the sediments approximately 60 by 80 yards in size. This comprises an anticline of impure limestone in kyanite-schist. The attitudes of folds and foliation in this block parallel those of the nearby wall rock. The block, however, has suffered no alkaline injection such as is common in the wall rock. The serpentinite has probably formed a chemical and physical

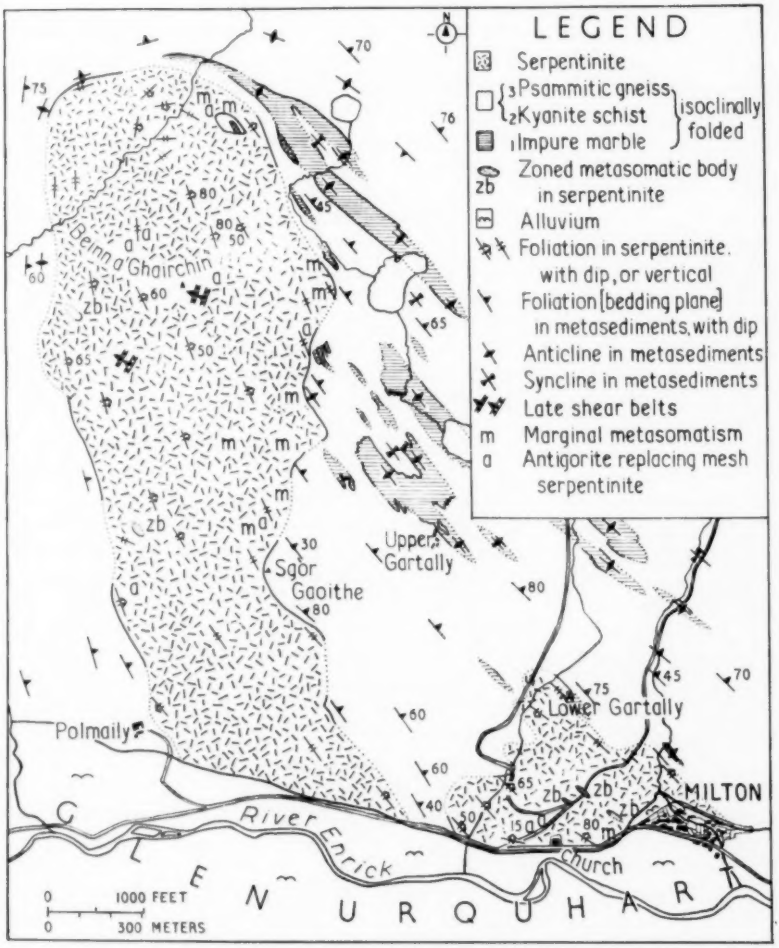


Fig. 1-B. Sketch map of the serpentinite mass in Glen Urquhart.

barrier to such injection. This also suggests that there is no underground connection of the block with the wall rock.

The serpentinite mass, although probably joined at depth, is exposed in three distinct masses, two large, and one a small sheet intruded between a limestone and a kyanite-schist bed (see map, fig. 1). In rising the ultrabasic probably found the sediments still in a plastic state for it seems to have deformed them plastically. In sediments at the north of the mass the axial plane of an isoclinal fold has been folded through 180°, presumably by the serpentinite. The possible mechanics of these structures will be discussed in a paper on the sediments.

For reasons discussed below it seems likely that the body rose as a mush of olivine and enstatite crystals with interstitial water vapor. Such an intrusion would be expected to show lines of shear parallel to its movement direction. In fact the serpentinite is foliated, but for this several mechanisms could be postulated. Stresses which produced folding of the surrounding rocks must be excluded since the mass cuts these folds. A general shearing long after solidification is also unlikely since the shear foliation affects all the mass but none of the wall rock. It therefore seems likely that intrusion, shearing, and serpentinization took place roughly together. Nearly all the shearing strikes with the long axis of the mass and dips steeply to the east-north-east. This is taken to be the direction from which the mass rose.

Near the summit of Beinn a' Ghairchin is a small series of shear belts striking northeast and dipping at 30° to 50° to the northwest. They vary from 4 inches to 2 feet in width, are intensely sheared, and abruptly truncate the intrusion foliation of the mass. They are composed of talc and magnesite with some chlorite and iron ore, and probably belong to the Older Granite metasomatic episode.

MINERALOGY

Serpentine minerals.—A detailed discussion of the structure of the serpentine minerals is beyond the scope of this paper. Work on these structures is at present going forward rapidly, and is not yet complete. For the present study it suffices to distinguish between platy and fibrous serpentine minerals and to examine the probable effects of their structure on their optics.

Identification of the minerals has been based chiefly on charts run on the Norelco X-ray spectrometer of the Geophysical Laboratory, Washington, kindly prepared by Dr. H. S. Yoder, Jr. Pattern differences between synthetic and natural chrysotile on the one hand and natural antigorite on the other have already been shown by Yoder (1952, p. 575-576, fig. 4). These patterns are repeated in the Glen Urquhart materials. In addition I am indebted to Dr. Yoder for patterns of synthetic aluminous serpentine (no.E.153) and of natural leuchtenbergite (clinochlore) from New Gabbs, Nevada, for use as standards of comparison (Yoder, p. 576-579, fig. 5).

Antigorite patterns are given in figure 2. The first three are the classic antigorites described by Bonney (1908), Aruja (1944), and Zussman (1953; 1954).[1] D is a coarse-grained, flaky antigorite of apple-green color from Glen Urquhart, described below (pl.2-A,-C). E is a very fine-grained variety associated with the last (pl. 2-D). It has the massive jade-like appearance and apple-green color formerly used to distinguish the variety "bowenite." The pattern confirms Selfridge's finding (1936, p. 501) that "bowenite" is a form of antigorite. These patterns are also similar to that of the Caracas mineral (Yoder, 1952., fig. 4C, p. 576).

In figure 3 are shown patterns from A, synthetic aluminous serpentine; B, leuchtenbergite (referred to above); C, cross-fiber chrysotile from Glen Urquhart; D, a "bastite" pseudomorph; and E, the mesh-structure groundmass of a "bastite"-serpentinite. The Glen Urquhart chrysotile has essentially

[1] According to Dr. J. Zussman (personal communication) pattern C is not representative of the Mikonui material, several peaks being absent.

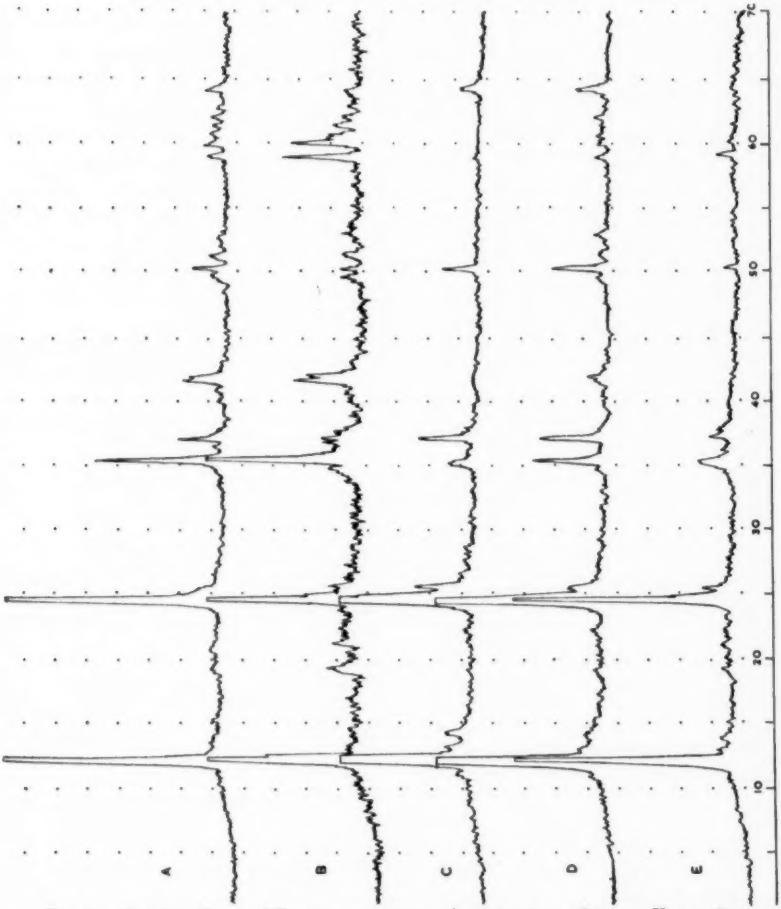


Fig. 2. Powder X-ray diffraction patterns of antigorites. Copper K-α radiation. Spacing in degrees 2θ.

A. Antigorite, Val Antigorio, Piedmont; Harker Collection, no. 19,710.
B. Antigorite, Griffin Range, Hokitika, N.Z.; H.C., no. 19,343.
C. Antigorite, Cross River, Mikonui, N.Z.; H.C. no. 11,566.
D. Antigorite, Milton, Glen Urquhart; H.C., no. 76,095.
E. Antigorite ("Bowenite"), Milton, Glen Urquhart; H.C., no. 76,094.

the same pattern as synthetic and natural chrysotiles given by Yoder (1952, figs. 4A and 4B, p. 576). The pattern for "bastite" can be seen to be closer to that of chrysotile than to that of antigorite. This is in agreement with the findings of Selfridge (1936). It is contrary to the views of Hess, Smith, and Dengo (1952), and Leech (1953), and to the data of Winchell (1951, p. 386).[2]

[2] In a paper read to the Mineralogical Society on 3rd November, 1955, E. J. W. Whittaker and J. Zussman have grouped the Glen Urquhart "bastite" with a new serpentine mineral species, lizardite.

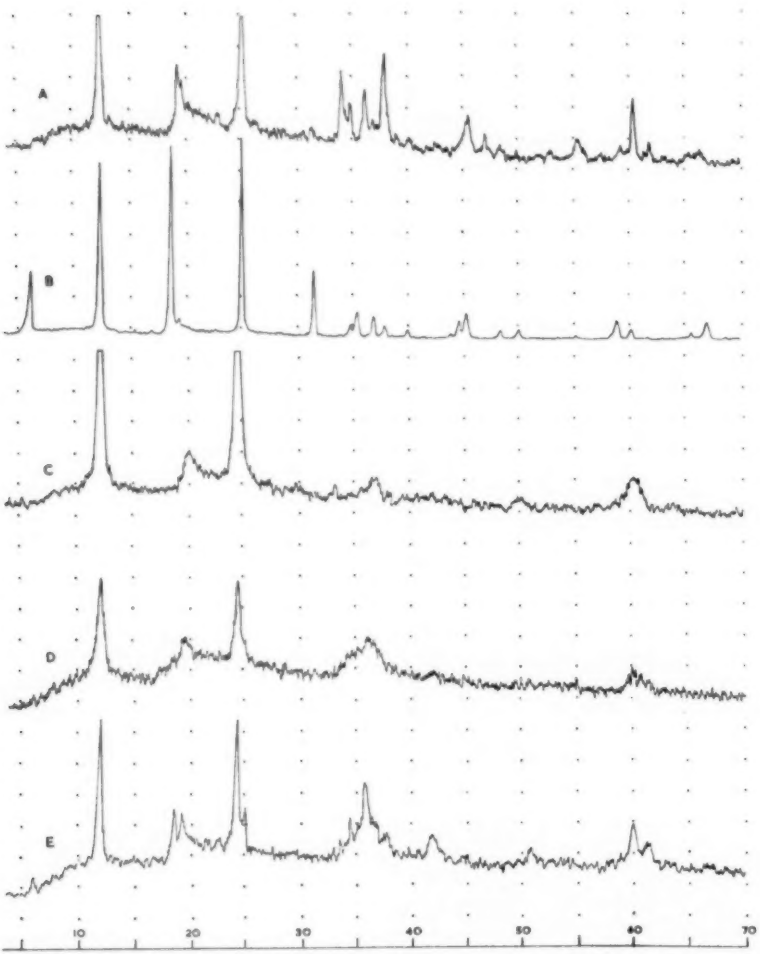


Fig. 3. Powder X-ray diffraction patterns of serpentine and chlorite. Copper K-α radiation. Spacing in degrees 2θ.

A. Aluminous serpentine no. E. 153 (synthetic): (Yoder, 1952, p. 579).

B. Leuchtenbergite (clinochlore), New Gabbs, Nevada.

C. Cross-fiber chrysotile, Milton, Glen Urquhart; H.C., no. 76,140.

D. "Bastite," Polmaily, Glen Urquhart; H.C., no. 76,113.

E. Mesh-texture groundmass of "bastite"serpentinite, Polmaily, Glen Urquhart; H.C., no. 76,113.

Figure 3-E is the pattern of the groundmass of the serpentinite from which the pattern of "bastite" pseudomorphs (fig. 3-D) was also obtained. This groundmass has the typical mesh texture described below. A few relict olivine crystals occur in the cores of meshes. They are probably too scarce to

affect the powder pattern. Chlorite occurs more abundantly than the olivine; talc and tremolite are present, but in minute amounts. The chlorite in the groundmass is identified in the following peaks of figure 3-E: 6°, 18.4°, 25°, (2θ). The peak at 31.5° in clinochlore (fig. 3-B) is absent. The rest of the pattern could contain chrysotilic serpentine or aluminous serpentine (compare with figs. 3-C, 3-A, 2-A—E). Chrysotilic serpentine seems present in some quantity. Aluminous serpentine, which has not before been reported in nature, may be present on the evidence of the pattern but the low Al_2O_3 content of the rock (1.64%, cf. table 4) argues against this. The alumina might all be held in the chlorite. Unfortunately, insufficient samples were sent to Washington fully to eliminate preferred orientation in the X-ray spectrometer patterns. Dr. Yoder comments that they are not good enough patterns to provide measured spacings, but are adequate to distinguish between antigorite, chrysotile, Al-serpentine, clinochlore, etc.

Measured optical constants of antigorites from Glen Urquhart are given in table 1 below.

TABLE 1
Optics of Antigorite

Specimen number	Refractive indices in sodium light ± .002	Optic axial angle in white light
76,095*	$N_x = 1.564$	$2V_x = 59° 30'$
	$N_y = 1.568$	(average of 10 measurements)
	$N_z = 1.573$	Dispersion r>v distinct
76,279	—	$2V_x = 61°$, (average of 4 measurements)
76,137	—	$2V_x = 60.5°$, (average of 2 measurements)

* All specimen numbers refer to the Harker Collection, Department of Mineralogy and Petrology, Cambridge, England.

Two optical orientations have been given for antigorite: (1) that of Winchell (1951), and Hess, Smith, and Dengo (1952); (2) that of Zussman (1954) (see fig. 4). In the first the optic plane is parallel to (010), and the acute bisectic X is sensibly normal to (001). In the second the optic plane is normal to (010), Z is parallel to *b*, and X and Y are nearly parallel to *c* and *a* respectively. Zussman's orientation must be accepted since the crystallographic directions are confirmed by the X-ray study. The first orientation may also be true but appears to lack X-ray structural control. Zussman's material from Mikonui shows two cleavages (or partings) on basal planes, namely (100) distinct, and (010) subordinate. With the perfect (001) cleavage this causes it to break up into rectangular plates elongated parallel to the *b* axis. These fragments will all have positive elongation. Winchell, and Hess et al. record only a (100) parting apart from the perfect (001) cleavage.

The Glen Urquhart antigorite possesses the perfect (001) cleavage. It has a prominent (100) parting and a subordinate (010) parting making the mineral break into rectangular plates. The long axes of these plates are parallel

to *b* according to recent X-ray studies (J. Zussman, personal communication, 1955). The optic axial plane is parallel to (100), Z appears to be in the (001) plane with X close to *c*, Y close to *a*. This antigorite therefore has orientation (2) as with the Mikonui mineral. A suggestion of a 30° or 60° parting in the [001] zone is visible in some crystals. The Glen Urquhart antigorite shows a distinct anomalous bluish tint in crystals with a low path difference, as does the Caracas mineral (Hess, Smith, and Dengo, 1952).

The optic orientation of fibered serpentine minerals is clearly more complex than that of platy antigorite. Two fiber types have been distinguished in X-ray and electron microscope studies (Bates, Sand, and Mink, 1950; Noll and Kircher, 1951; Nagy and Bates, 1952; Zussman, 1953, 1954; and others). These are (1) (001) planes curved about *a*, with a 5.3 Å repeat distance along the fiber axis; these can form perfect tubes (in the case of chrysotile asbestos). Concentric tubes and tubes with split ends are recognizable in electron micrographs (e.g. Bates, Sand, and Mink, 1950). (2) Fibers with a 9.2 Å repeat along their axes. Zussman (1954) has found that type (1) is restricted to chrysotile and serpentine of Selfridge, type (2) to antigorite of Selfridge and suggests that the latter fiber axis may derive from curving of (001) planes about *b*.

Three fiber types are recognized in optical studies, namely, *alpha serpentine* with negative elongation and *gamma serpentine* with positive elongation (Tertsch, 1922), and thirdly, somewhat curved antigorite (noted in addition to the last two by Selfridge, 1936) also with positive elongation. If the initial (001) plane has the Mikonui orientation then two of the three fibers can be derived from that orientation by curvature (fig. 4). If the (001) plane is curved about *a* then, in testing the optical elongation, Y (vibrating sensibly parallel to the fiber axis) will be compared with a mean of X and Z, and will be greater than that mean since the mineral is optically negative. The fiber will have positive elongation. This would explain the optical orientation of chrysotile asbestos and gamma serpentine. If the (001) plane is curved about *b* then Z (vibrating parallel to the fiber axis) will be compared with X and Y and the fiber will again have positive elongation. This would explain why antigorite with some curvature (i.e. splintery, cf. Selfridge, 1936, table 4, "picrolite," "picrosmine," etc.) has positive elongation similar to platy (e.g. Mikonui) antigorite. Very small amounts of alpha serpentine hand picked from mesh serpentine and examined by Dr. J. Zussman give X-ray powder

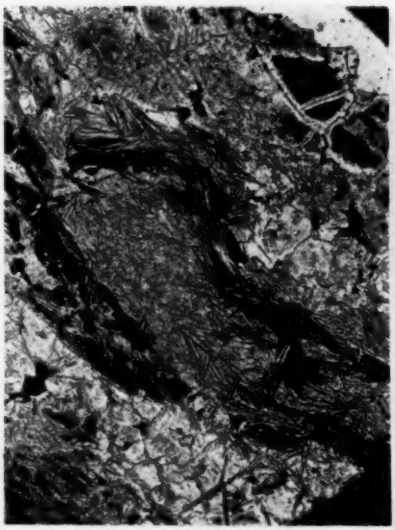
A. "Bastite"-serpentinite, Polmaily. A large "bastite" showing fibration parallel to the length of the prism. Mesh-texture groundmass with a few relict olivines at center. Ordinary light. X-ray patterns of figure 3-D and E, and analysis, table 4-I are from this rock. Plane light (no. 76,113).

B. Enstatite relict in "bastite," Polmaily. Note fiber direction in the "bastite" parallels the distinct (010) parting of the pyroxene. A prism of tremolite at lower right. Plane light (no. 76,103).

C. Mesh-texture groundmass under high power, Polmaily. Bipartite cross-fiber collars of alpha serpentine surround near-isotropic cores of matted gamma serpentine in which hourglass structure is visible in some cases. Crossed nicols (no. 76,113).

D. Chlorite-tremolite-ore pod in serpentinite, Sgór Gaoithe. Chlorite and tremolite sheathed with magnetite. Cores of meshes at top right and lower left have abundant ore dust and a turquoise tint. Analysis, table 6-II is from this rock. Plane light (no. 76,110).

PLATE I



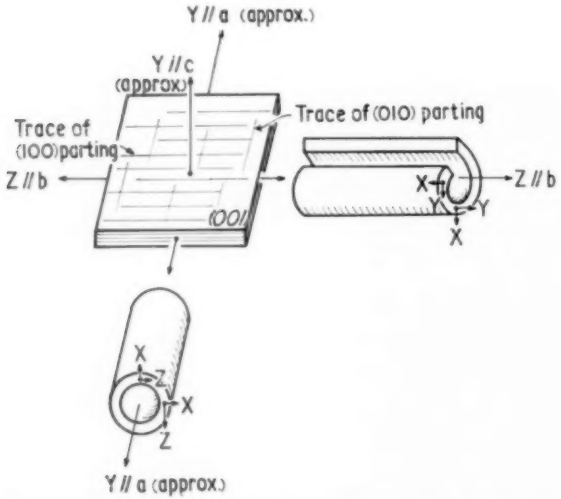


Fig. 4. Supposed optic orientation of fibrous serpentine derived from platy serpentine by curvature about the *a* and *b* crystallographic axes. The platy serpentine in this figure has the optic orientation of the Glen Urquhart and Mikonui antigorites. Zussman (1954) shows that curvature about *a* is restricted to chrysotilic minerals, curvature about *b* to antigoritic minerals as defined by Selfridge (1936). Note that the elongation (positive or negative) of fibers about *a* would depend on the sign of 2V; the elongation of fibers about *b* must be positive.

patterns of chrysotile rather than antigorite. The material was unsuitable for a direct investigation of the fiber repeat distance, but seems likely on the above grounds to be fibered about *a*. If alpha serpentine is fibered about *a* its negative elongation could be explained by a change from 2V (−) to 2V (+). If the curved plate was optically positive Y would be less than the mean of X and Z (see fig. 4), and the fiber would have negative elongation. An explanation here exists for the greater observed birefringence of chrysotile asbestos than that of gamma serpentine in the meshes. $2V_z$ in chrysotile asbestos has presumably a larger value than in gamma serpentine. There is probably a complete series from these values through $2V_z = 90°$ in the often-seen apparently isotropic fibers, to $2V_z$ acute in alpha serpentine. It is not known whether this postulated variability in 2V would be due to slight compositional (or to some other) variations. The mere fact of fibering makes it impossible

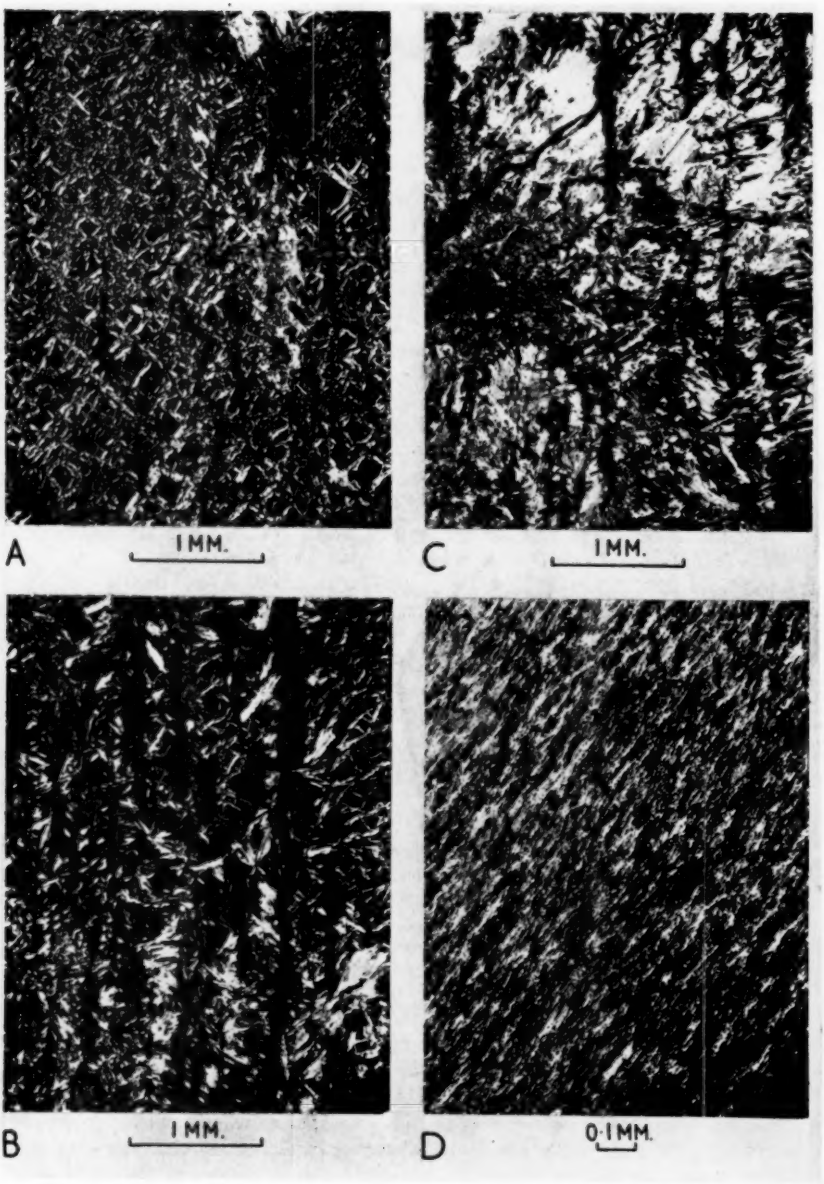
A. Relict of mesh-texture serpentinite enclosed in antigorite-serpentinite, Milton. Note dark lines diagonal to the very regular rectangular meshes. Crossed nicols (no. 76,095).

B. Partial replacement of mesh-texture serpentinite by antigorite. Diagonal lines here clearly occupied by antigorite. Crossed nicols. Same slide as A.

C. Total replacement of mesh-texture serpentinite by antigorite. Diagonal lines persist X-ray pattern in figure 2-D. Crossed nicols. Same slide as A.

D. Fine-grained jade-like antigorite ("bowenite"), Milton. Shows late shearing of pre-existing antigorite. Fissility (shown by a crack) parallel to the shear foliation. X-ray pattern in figure 2-E. Crossed nicols (no. 76,094).

PLATE II



to measure separately the two refractive indices vibrating normal to the fiber direction in serpentine or chrysotile (cf. Winchell, 1951, p. 379).

In some of the "serpophite" cores of the serpentine meshes is considerable ore dust, probably chromiferous. Occasionally this has appeared to react with the fine serpentine fibers of the "serpophite" to form a distinct mineral. This has fair relief, refractive index considerably above serpentine, and is anisotropic with low birefringence. The color is a vivid turquoise which masks the low order interference colors. No cleavage has been seen. Occasionally (no. 76,279) minute isotropic granules occur within the green mineral. They are believed to be pyrope garnets. The green mineral is unidentified (cf. Benson, 1918, p. 726). The cross-fiber chrysotile asbestos grows in typical sinuous crosscutting veins in which the fibers maintain strict parallelism around the curves. The maximum length of the fibers (i.e. vein width) is 1 mm. As seen above the mineral has a normal powder pattern and corresponds to serpentine fibered about *a* with positive elongation. The apparent birefringence is greater than in the analogous gamma serpentine of the meshes.

A few examples of slip fiber chrysotile occur. In one case the fibers are sky blue, slightly undulating in growth, and brittle. They reach 15 cm in length. Their interference colors are high in the first order. The mineral is of earlier growth than the cross fiber since it is speared through by antigorite.

Olivine.—Magnesian olivine (as relicts in mesh cores) is widespread. Before serpentinization it must have formed the bulk of the rock. Optical constants (table 2) indicate that it is a forsterite with a composition around Fa_1 (Poldervaart, 1950).

TABLE 2

Optics of Olivine, Orthopyroxene, and Amphibole in the Serpentinite

Number	Mineral	Refractive index[1]	Optic axial angle[2]	Extinction angle (2) Z∧*C* on (010)
76,090	Olivine	—	$2V_z = 85°30' \equiv Fa_1$[3]	—
76,103	Olivine	$N_y = 1.662 \equiv Fa_2$	$2V_z = 85°00' \equiv Fa_3$[4]	—
76,103	Enstatite	$N_z = 1.670 \equiv Of_1$	$2V_z = 75°00' \equiv Of_7$[5]	—
76,090	Tremolite	—	$2V_x = 80°00'$[5]	15°00'[5]
76,103	Tremolite	—	$2V_x = 78°00'$[5]	18°00'[5]

(1) Measured at 20°C. in sodium light: estimated error ± .002

(2) Measured on the Universal Stage using white light.

(3) Average of 4 measurements } Olivine molecular values read from graph of

(4) Average of 5 measurements } Poldervaart (1950).

(5) Average of 3 measurements. Orthopyroxene molecular values read from graph of Hess (1952).

Enstatite.—The universal and common "bastite" pseudomorphs show the quantity of enstatite held in the unaltered rock. In three cases only relicts of enstatite have been found within "bastite" individuals in every stage of replacement by serpentine (pl. 1-B). This shows that a linear direction in the "bastite" parallels the distinct (010) parting of the orthopyroxene. Winchell (1951, p. 386) describes this linear direction as the (001) cleavage of platy (antigorite) serpentine. Reasons are given above, however, for believing

that this "bastite" is chrysotilic. The linear direction probably consists of bundles of fibers following the (010) parting of the pyroxene (see also F. C. Phillips, 1927, p. 628). The orthopyroxene is colorless and non-pleochroic. Its optics (table 2) suggest a composition around Of_6 (Hess, 1952). It seems that the FeO/MgO ratio of the enstatite exceeds that of co-existing olivine (see above) in these rocks. This agrees with the findings of Ramberg and DeVore (1951, p. 196). They find that the above relationship exists in extremely magnesian rocks carrying the two minerals. All others have the reverse relationship.

Tremolite and actinolite.—Much tremolite in the mass is clearly secondary, and is one of the commonest products of hydrothermal alteration. Some of the fine-grained material in the groundmass accompanied the serpentinization of the ultrabasic. It is not always possible to separate the two under the microscope although the second generation amphibole appears to have the greater extinction angle. The fine-grained material forms trains and clusters of colorless prisms like bacilli. A few larger crystals up to 1 mm long occur (pl. 1-B, lower right corner). These crystals show some serpentinization, and so belong to the earlier generation of amphibole. Some of their optics are given in table 2. In the second generation fine-grained amphibole (especially in chlorite-tremolite pods) increases, and later large "spearing" porphyroblasts are formed, up to 1.2 cm in length. These are characteristic of the marginal hydrothermal bodies. They have a negative sign and extinction $Z \wedge c$ from 20° to 25°, and are colorless. Amphiboles are often rotted to an opaque, brownish material. Lozenge-shaped cross sections of this material in some slides are the only indication of the former presence of amphibole.

Anthophyllite.—Rhombic amphibole up to 2 cm long occurs in many of the marginal hydrothermal bodies. Its extinction is usually straight. When it is oblique in oblique-cut sections it never reaches the ordinary clinoamphibole extinction angles. The optic axial angle is close to 90°, and is acute about $Z = c$. The Bx_a figure is thus found in basal sections.

Chlorite.—This mineral is abundant in the serpentinite. Like tremolite, with which it is closely associated, it largely derives from the period of hydrothermal alteration, but fine flakes in the groundmass may have crystallized with the early tremolite. Late chlorite occurs in the chlorite-ore pods and in almost pure chlorite rocks of the marginal bodies with crystals up to 6 mm across. Commonly the chlorite has buff polarization colors and is optically positive ($2V_z = 5°$ ca). The refractive index on (001) plates is $N_y = {}^{p}N$ 1.582 (± .002). Birefringence is low (around 0.001). These optics suggest pennine, close to diabantite (Hey, 1954, p. 284, figs. 1a, 4). The predominant optically positive chlorite grades through an apparently isotropic condition to optically negative chlorite with ultrablue polarization colors and $2V_x$ around 5°. The optically negative chlorite occurs rimming the positive, as bands parallel to (001) in the positive, and as cores within the positive chlorite.

In some of the chlorite-ore pods (e.g. 76.282) the chlorite is associated with chromite—suggesting that it may contain some chromium.

Talc.—This is a common mineral. It occurs largely in the marginal hydrothermally altered bodies, but is also found in unmodified serpentinite. Large scaly plates up to 1.5 mm across, and sheaf-like pseudomorphs after anthophyllite are typical of the first type. Talc occurring as thin selvedges around "bastites" appears to be an original feature dating from the serpentinization. The formation of these talc rims can be explained with reference to Bowen and Tuttle's work (1949, fig. 2, p. 447) where it is clear that cooling of enstatite plus excess water vapor could give rise to the assemblage serpentine + talc + vapor below 500°C. Micro-crumpling normal to the basal planes, intersecting varied bands of interference colors in those planes, produces a tartan effect.

Carbonates.—Magnesite (or breunnerite) is common in the marginal bodies. It occurs in veins and in the groundmass. It is brown in color, with one refractive index just less than Canada balsam, the other much greater. The birefringence is high, and the mineral is uniaxial negative. Lamellar twinning is absent and cleavage is rare. The groundmass magnesite is of earlier formation than the veinstuff.

Other minerals.—Prehnite, xonotlite, phlogopite, and vermiculite also occur in marginal hydrothermal bodies.

Accessories.—Apart from the above minerals calcite, chalcedony, garnet, bowlingite, pyrite, magnetite, hematite, ilmenite (with "leucoxene"), and chromite all occur in minor amount. Calcite occurs with magnesite in the groundmass and in veins. Chalcedony occurs with white opaque veinstuff in late crosscutting veins. It appears as small spherulites with perfect polarization crosses. Opaline silica is sometimes associated with the chalcedony. The opaque veinstuff whilst not identified may prove to be saponite. Small garnets 0.05-0.1 mm in size have already been noted. In their magnesian environment they are probably pyropes. Bowlingite appears in many slides as a red-brown micaceous alteration product after olivine in the cores of the meshes. It has a refractive index slightly greater than that of serpentine and a birefringence around .020. These data exclude the possibility of iddingsite whose refringence and birefringence are considerably higher. Iddingsite, moreover, usually forms from strongly fractionated iron-bearing solutions rather than in a magnesian environment.

Chromite with red-brown translucent cores occurs amongst the ore minerals, also skeletal ilmenite in some slides, and much magnetite. A small amount of pyrite is seen in reflected light. Its presence is confirmed in the sulphur content of the two analyses below (table 4.I and 6.II).

PETROLOGY OF UNINJECTED SERPENTINITE

Parageneses.—Serpentinite parageneses of rocks unaffected by subsequent hydrothermal alteration are given in table 3. The serpentine minerals are here divided under serpentine (α and γ varieties), chrysotile (cross-fiber asbestos veins), and antigorite since presumably their stability fields differ. Thus serpentine-antigorite and even perhaps serpentine-chrysotile may be regarded as incomplete transformations or disequilibrium assemblages.

Olivine and enstatite are present as relicts, and assemblages in which they occur must also be out of equilibrium. On this basis only nos. 6, 9, and 10

may be equilibrium assemblages following the serpentinization of the mass. Veining by chalcedony implies lack of equilibrium since at least theoretically it should react with serpentine to form talc. The only other equilibrium assemblage is no. 24.

TABLE 3

Parageneses of Uninjected Serpentinite

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24
Serpentine	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x		
Chrysotile				x			x	x			x	x		x			x		x	x	x	x		
Antigorite																		x	x	x	x	x	x	x
Olivine	x	x	x	x	x																			
Enstatite					x																			
Tremolite	x		x	x	x				x	x	x	x	x	x	x	x					x	x	x	
Chlorite	x	x	x	x	x	x	x	x	x	x	x		x	x	x	x	x	x	x	x	x	x	x	
Talc		x	x	x	x			x		x	x	x										x	x	
Magnesite												x	x		x									
Chalcedony													x	x										
Calcite																x	x			x				
Garnet																						x		

Chemistry and origin.—In table 4 are given the chemical analysis, trace elements, and norm of a "bastite" serpentinite with mesh-texture groundmass together with the analysis and norm of similar rock from Central Sutherland. Analysis I is typical of many serpentinites and compares with Analysis II. The latter is from an area of "rocks of Lewisian type," thought by Read (1931) to be an integral part of the Moine Assemblage. With the disproof of a Lewisian age for many, if not all the Central Ross-shire "inliers," more serpentinite bodies are becoming recognized as intrusive into Moine rocks. As a group these bodies comprise a serpentinite belt along the axis of the Scottish Highlands. If the Glen Urquhart evidence applies generally they were intruded between the acme of folding and the Older Granite injection. They are to be distinguished from the Scyelites and Ach'Uaine ultrabasics, which belong to the group of Newer Igneous rocks. The belt is not localized along fault lines, as are The Great Serpentine Belt of New South Wales—Queensland (Benson, 1913-1918; Wilkinson, 1953) or The Ultrabasics of the Highland Boundary (Anderson, 1947). It is more like the Appalachian belt (Pratt and Lewis, 1905) although on a smaller scale.

TABLE 4
Serpentinite Analyses

	I	II		Ia	IIa	Ib	
SiO_2	38.15	37.53				Li	tr.
Al_2O_3	1.64	0.72	or	2.22	—	Rb	tr.
Fe_2O_3	4.51	5.12	ab	—	1.57	Cs	tr.
FeO	2.35	1.78	an	3.34	1.11	Tl	tr.
MgO	37.25	37.99	C	0.31	—	Sr	tr.
CaO	0.65	1.32	di	—	4.32	Ba	tr.
Na_2O	0.07	0.18	hy	24.30	22.80	Ga	tr.
K_2O	0.40	0.03	ol	48.40	49.28	In	tr.
H_2O+	13.61	11.75	mt	6.50	5.10	Sc	tr.
H_2O-	0.66	0.68	cm	0.15	0.45	Yt	tr.
TiO_2	0.03	0.09	pyr	0.82	0.60	La	tr.
P_2O_5	0.04	—				Zr	tr.
MnO	0.08	0.17				Sn	tr.
CO_2	tr.	2.04				Pb	tr.
S	0.18	—				V	15.
FeS_2	—	0.29				Cr	1500
Cr_2O_3	0.22*	0.33				Mo	tr.
(Co,Ni)O	0.22*	0.08				Co	65
	100.06						
Less O≡S	0.07					Ni	1500
	99.99	100.10				F	nil.
Sp.Gr.	2.75						

* From spectrographic determination.

I. Olivine-bearing "bastite"-serpentinite. Crag N.E. of Polmaily House, Glen Urquhart. (Harker Collection no. 76,113). Analyst G. H. Francis.

II. "Bastite"-serpentinite. Allt Dionach Caraidh, Central Sutherland. (Read, 1931, p. 79.) Analyst, B. E. Dixon.

Ia. C.I.P.W. norm of I.

IIa. C.I.P.W. norm of II.

Ib. Spectrographic determination of minor elements in Analysis I (parts per million). 'tr' means present but below the limits of quantitative determination. Spectrography, Dr. S. R. Nockolds.

Ross, Foster, and Myers (1954) have recently summarized opinion on the origin of dunite and have given strong evidence for supposing a similar origin for dunite nodules in basaltic rocks. This origin is now generally believed to be the periodotite layer of the Earth's crust thought to lie beneath the Mohorovičić discontinuity (Hess, 1938; Tilley, 1955). Certain other ultrabasic bodies not entirely free from feldspar and/or associated with basic rock such as those of Skye, the Bushveld Complex, Stillwater, are doubtless in a separate category, formed by accumulation of early-formed olivine and enstatite from basic magma.

The distinguishing features of the orogenic ultrabasics of the belts are partly their environment and partly their chemistry. Hess (1938) believed these ultrabasic bodies to rise as magma, and Wilkinson (1953) has given further evidence for fluidity in his study of serpentinite breccias in Queensland. The laboratory work of Bowen and Tuttle (1949), however, leaves little if any theoretical basis for a liquid of the composition of olivine + water, which is unable to effect notable contact alteration (chemical or thermal) of the country rock. The pod-like shape and sheared fabric of ultrabasic bodies also argue their origin by the intrusion of a mush of olivine crystals with or without enstatite and clinopyroxene crystals. Ross, Foster, and Myers (1954) have reviewed the favorable field and textural evidence for intrusion by a mush of crystals with reference to North Carolina, New Zealand, and Swedish occurrences. The criteria of these authors for solid intrusion apply for the Glen Urquhart ultrabasic mass. It has a simple pod-like outcrop, without ramifying veins or apophyses, it has caused no noticeable contact-alteration of the country rock, and it has a sheared fabric. A final point is that these ultrabasics occur without any associated basic rock.

The second criterion, the chemical one, also separates ultrabasics of the belts, the "alpine" type of Benson (1926), from crystal accumulative types. Hess (1938) gives curves to show the difference in frequency distribution of Mg/Fe molecular ratios for ultrabasic types of differing origin. The "alpine" type is the most magnesian with ratios at a maximum between 9 and 10. The two Scottish ultrabasics are unusually magnesian with ratios of 15.3 and 16.1 respectively. They have Al_2O_3 and CaO in small amount, also agreeing with the "alpine" type. Analysis I is very poor in trace elements other than the expected chromium and nickel.

Serpentinization.—The serpentinization of the mass has apparently given rise exclusively to the "bastite"-serpentinite with mesh-texture groundmass. From the study of relict minerals it is clear that enstatite has altered to "bastite" and olivine to mesh serpentine. It is not now possible to say whether the original olivines were as large as the enstatites or whether the latter were indeed phenocrysts. In most cases the olivine component was in excess of the orthopyroxene. Johannsen gives no specific name for such rocks (1938, v. 4, pt. II, p. 423), but they come under the general heading of olivinites. They are close to the saxonites.

A few facts are relevant to the serpentinization. The ultrabasic mass was emplaced after the regional metamorphism into crystalline schists poor in water (kyanite-schist 0.73%, paragneiss 0.40% total water). These analyses come from typical rocks. There is no field or mineralogical evidence that the ultrabasic took water from its wall rock or added water to it. Absolutely normal kyanite-schist and "bastite"-serpentinite occur side by side at some contacts. It is also clear that water for serpentinization was not provided by the Older Granite metasomatism since the effect of this on the ultrabasic mass has been the alteration of *pre-existing* serpentinite to assemblages of talc, actinolite, chlorite, etc. This excludes the suggestion of Du Rietz (1935) and Bowen and Tuttle (1949) that hydrothermal waters from granites are responsible for serpentinization, at least in the Glen Urquhart example. Since

water apparently neither preceded the arrival of ultrabasic rock nor followed it, it seems likely that it accompanied it. A mush of olivine and enstatite crystals must have risen accompanied by water vapor (of unknown provenance). When the movement was virtually complete, cooling would bring the crystals and vapor into the stability field of serpentine (Bowen and Tuttle, 1949) causing the serpentinization. Talc rims around bastites would also be formed at this stage (see under *Talc*, above). The serpentinization probably marked out lines of crushing from the previous movement episode, making a visible foliation. Enstatites which had escaped crushing would give rise to undeformed "bastites" whilst crushed enstatite would be unrecognized in the serpentinized groundmass. This may meet Hess' objection to solid intrusion (1938, p. 326) that "bastites" are usually undeformed. (Coarse-grained enstatite is known also in unserpentinized ultrabasic intrusions which have presumably risen as crystal aggregates.) Late adjustments of the mass at Glen Urquhart after serpentinization have locally sheared mesh and "bastites" alike forming the slaty rocks (see figs. 5-B and C).

Petrography of "bastite"-serpentinite with mesh-texture groundmass.—This rock, the normal type of the mass, has a very clear development of trellis-like meshes of serpentine set with prismatic pseudomorphs in serpentine after enstatite ("bastites"). Olivine and enstatite may persist as relicts or may be completely converted to serpentine. Cross-fiber chrysotile veins are frequent. Chlorite and tremolite occur as sparse threads and trains in the groundmass. Magnetite or chromite grains or dust are often concentrated along mesh "collars" or in mesh cores. This sooty dust sometimes seems to have reacted with the serpentine of the cores to form an unidentified turquoise-colored material. In some mesh cores are patches of red-brown bowlingite.

The nature and origin of "bastite" pseudomorphs is discussed in the mineralogy section above. The pseudomorphs vary between 0.5 and 2.5 cm in length and 0.2 and 0.8 cm in breadth (pl. 1-A, B). Selfridge (1936, pl. II, fig. 2) figures "bastite" from Baste, Harz, Germany. This resembles a rather perfect development of the mesh-texture after olivine, described below (see fig. 5-A). Other examples from Baste show the same linear arrangement of fibers as the Glen Urquhart material. Both types from Baste are represented in the Harker Collection at Cambridge (nos. 12,839, and 18,880). In some slides the replacement of a relict enstatite to form "bastite" is clearly seen (pl. 1-B). One "bastite" contains small patches of mesh serpentine, probably representing olivine ophitically held in enstatite before the serpentinization.

The optical nature of serpentine fibers is discussed in the mineralogy section above. The arrangement of these fibers in the meshes has been described by Tertsch (1922) and Selfridge (1936). According to Tertsch two types of texture (or structure) occur: (1) *Mäschenstruktur*, in which the rims (collars) of the cells are of gamma serpentine and the cores are of alpha serpentine; (2) *Fensterstruktur*, in which the collars are of alpha serpentine, the cores of gamma serpentine. All the Glen Urquhart examples correspond to (2). Selfridge did not find any of this type in his study.

Typical meshes under high magnification are here illustrated (pl. 1-C). They are composed of bipartite collars of cross-fiber alpha serpentine and all

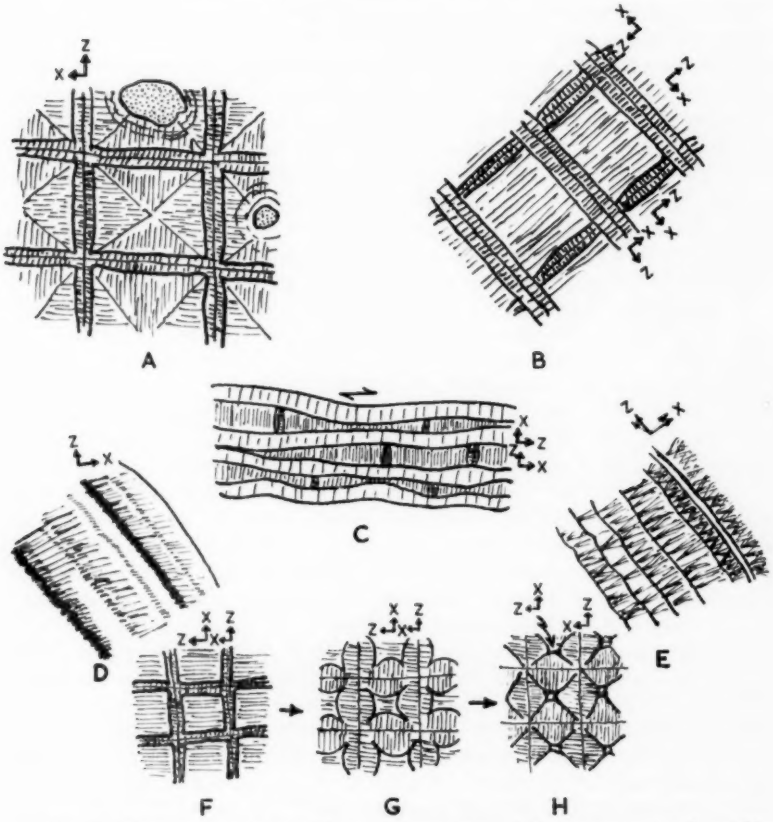


Fig. 5. Form and optic orientation of some types of fibrous serpentine from Glen Urquhart. Magnification about 100X (Diagrammatic). The directions of apparent greater and lesser ease of vibration in fiber groups are shown by X and Z respectively.

A. Normal mesh-texture serpentine with olivine relicts in some cores. Alpha serpentine in bipartite cross-fiber collars: gamma serpentine in the cores in hourglass arrangement (compare pl. 1-C).

B. Mesh-texture serpentine somewhat affected by shearing.

C. Mesh-texture serpentine greatly affected by shearing (direction shown).

D. Alpha serpentine in curtain-like, banded growth.

E. Alpha serpentine in sheaf-like, banded growth.

F, G, H. Progressive development of alpha serpentine of the mesh collars at the expense of gamma serpentine of the mesh cores.

but isotropic cores of gamma serpentine. The gamma serpentine is often in matted growth leading to isotropism of the aggregate. Apparent isotropism may also be caused by 2V passing through 90° as noted in the mineralogy section above. These apparently isotropic cores have previously been referred to an amorphous mineraloid, "serpophite." In other slides the fibers are more

regularly disposed to form an hourglass structure (fig. 5-A and pl. 1-C). In places where the rock is sheared by late adjustments after serpentinization the cross-fiber collars in the plane of shearing develop at the expense of those normal to it. This produces a new foliation more distinct than the intrusion foliation of the mass. This effect is shown diagrammatically in figure 5-B. The dominant collars cut across the subordinate, and the gamma serpentine fibers of the core are arranged normal to the shearing. Occasionally the late shearing of the serpentinite is so intense as to form a serpentine-slate. Under the microscope the mesh texture appears as in figure 5-C. It is interesting to note that antigorite is not formed in these conditions of strong shearing. Where it does form the relict mesh texture serpentinite shows no shearing at all.

Sometimes broad bands of alpha serpentine occur with curtain-like wavy extinction recalling the aurora (fig. 5-D). In other cases the bands are composed of rows of fibers growing in sheafs (fig. 5-E). In one rock (76.130) the growth of alpha serpentine collars at the expense of gamma serpentine cores can be traced (figs. 5-F, G, H.). This may indicate a change in the optic sign of the serpentine. The alpha serpentine appears in many cases to be the dominant and more stable of the two forms in Glen Urquhart.

Antigorite and its formation.—The occurrence and mode of origin of antigorite are so widely discussed that it is not possible to survey the literature here. A useful summary is contained in Benson (1918, p. 716-719). Crystallization of antigorite from a magma is a theory already abandoned at that date. Antigorite may directly replace olivine and pyroxene in a few instances but it usually replaces mesh serpentine. The latter is the case in Glen Urquhart. The formation of antigorite has frequently been pictured under conditions of high pressure (Benson, 1918, p. 716), and also of shearing stress (Hess, Smith, and Dengo, 1952, p. 74). The latter authors believe that a temperature higher than the green schist facies is also necessary for the formation of antigorite. Certain evidence discounts the formation of antigorite by pure thermal metamorphism, other evidence supports it. Against the thermal origin we find: (1) that Leech (1953) has found no antigorite to be formed from serpentine even up to the temperature at which olivine is regenerated; (2) antigorite did not form in any of the runs of Bowen and Tuttle in the system $MgO—SiO_2—H_2O$, although a range of probable temperatures and pressures up to 40,000 lbs/in^2 were used (1949, p. 443).

For the thermal origin: (1) Wilkinson (1953) has described the generation of antigorite from chrysotilic serpentine consequent on pure thermal metamorphism of an ultrabasic mass by nearby granites; (2) the matrix of regenerated olivine and enstatite in thermally metamorphosed ultrabasics in California (Durrell, 1940, p. 83; Macdonald, 1942, p. 244) is antigorite. Mesh serpentine forms only scattered remnants in these bodies, remote from their contacts. These ultrabasics are underlain by the batholith of the Sierra Nevada.

In Glen Urquhart antigorite has been found spearing through actinolite and talc-carbonate assemblages. It thus postdates these assemblages, formed by the Older Granite metasomatism. There is little direct evidence to show under what conditions these late-stage and localized antigorite masses formed.

The thermal theory is not supported by any known adjacent igneous rock. The shearing stress theory is somewhat better served. In a single hand specimen the transition from mesh serpentine to antigorite can be seen (pl. 2-A,-C). This is accompanied by lines diagonal to the rectangular meshes (pl. 2-A). Later they increase in size and number and contain fine-grained antigorite (pl. 2-B). Coarse, randomly oriented flame antigorite grows between the lines, and only relicts of mesh texture remain. Finally all the groundmass is converted to antigorite in typical radiating flame-like growth, whilst the diagonal lines persist (pl. 2-C). This coarse antigorite was used for the optical measurements (table 1) and the X-ray pattern (fig. 1-D). Close to the last occurs fine-grained jade-like antigorite, obviously much sheared. It is the type formerly called "bowenite" (fig. 1-E and pl. 2-D). These bodies of antigorite may have formed because of shearing but it is unwise to ignore the possibility that shearing and antigorite are found together merely by chance. In particular: (1) the transformation does not take place closely parallel to the diagonal (?) shear lines, large ball-shaped relicts of mesh-serpentine remain, surrounded by antigorite; (2) wide areas of antigorite between the diagonal bands have irregular flame-like growth with crystals quite unrelated spatially to the bands (pl. 2-B); (3) the highly sheared "bowenite" is generated from the shearing of the coarse antigorite, and not from mesh-serpentine.

PETROLOGY OF INJECTED SERPENTINE AND LATE VEINS

Parageneses.—The parageneses of injection-altered serpentinite (table 5) indicate the high-temperature zone of Phillips and Hess (1936). The actinolite and anthophyllite of these bodies and the vermiculite in injected sediments adjacent to the ultrabasic mass represent this stage. The formation of talc alongside, and from the amphiboles within the intrusion, and the chloritization of the vermiculite formed in adjacent sediments suggest transition to a lower temperature alteration zone. Anthophyllite formed early in the injection indicates a temperature higher than most examples noted by Hess (1933b, p. 646). The impersistence and small bulk of metasomatic rocks on both sides of the intrusive contact at Glen Urquhart suggest a weaker metasomatism than in Hess' American localities and in the Shetlands (Read, 1933; Amin, 1952).

Chemistry.—In table 6 are compared the normal "bastite"-serpentinite requoted from table 4 and a serpentinite containing chlorite-ore pods developed at an early stage of injection (pl. 1-D). Leech (1953, p. 36, 37, and pl. IX) describes veins of chlorite around ore (chromite) in British Columbia serpentinites. He does not believe that the chromite is hydrothermally introduced (cf. Fisher, 1929). A similar conclusion can be reached from the Glen Urquhart analyses which show less chromium in the injected than in the original rock (table 6b). One specimen (no. 76,291) consists of chlorite with abundant magnetite octahedra, minor quantities of garnet, and veins of chalcedony and magnesite. Similar rock is described by F. C. Phillips (1927, p. 639-641), and Harker (1939, p. 277). The present specimen may simply be a very large chlorite-ore pod.

The differences between columns I and II in table 6 show small but distinct changes following the alteration from a rock like I to what is now II

TABLE 5

Parageneses of Injected Serpentinite

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24
Serpentine	x	x	x																					
Chrysotile								x	x											x			x	
Antigorite				x	x		x	x	x	x														
Olivine			x																					
Tremolite				x																				
Actinolite		x			x										x	x	x	x	x	x	x			
Anthophyllite	x		x				x	x				x	x	x	x									
Chlorite	x	x	x	x				x	x	x	x		x	x		x			x	x	x	x	x	
Talc	x	x	x					x	x				x	x	x				x		x	x	x	
Magnesite					x		x	x	x		x			x				x	x		x	x	x	x
Chalcedony									x						x					x				x
Calcite																								
Garnet									x												x			
Prehnite									x															
Xonotlite																				x				
Phlogopite																								
Vermiculite										x							x							

by the Older Granite injection metasomatism. Increase of silica, alumina, and lime are most noticeable. Magnesia and water have decreased. Magnesia has diminished relative to increases in lime and alumina (e.g. in the new-formed amphiboles). Water has diminished by the formation of less-hydrated minerals (chlorite, tremolite) from serpentine. It is not clear whether this change has caused expulsion of water or a relative diminution of water; if the latter, this one-way transfer indicates an increase in volume of the rock on metasomatism, which is hard to verify. Both rocks are poor in minor elements other than chromium, vanadium, nickel, and cobalt. These all have apparently diminished on hydrothermal alteration. The C.I.P.W. norm shows the alterations clearly. Corundum is eliminated and hypersthene increases at the expense of olivine because of increased silica. Increased lime has brought in diopside and increased anorthite. The rise of alumina is taken up in increased normative feldspar.

This early stage of injection is the forerunner of the more copious injection forming the marginal bodies proper. The same oxides shown on the increase above (silica, alumina, and lime) must at a later stage have formed

the characteristic talc, chlorite, actinolite, and anthophyllite of the marginal bodies. A few discrete zoned bodies of hydrothermal origin cut the serpentinite. These will be described in another paper.

TABLE 6

Serpentinite Analyses to Show Incipient Metasomatism

	a			b			c	
	I	II		I	II		I	II
SiO_2	38.15	40.67	Li	tr.	2	or	2.22	0.56
TiO_2	0.03	0.16	Rb	tr.	—	ab	—	1.57
Al_2O_3	1.64	2.92	Cs	tr.	—	an	3.34	6.95
Fe_2O_3	4.51	5.35	Tl	1	—	C	0.31	—
FeO	2.35	2.46	Sr	tr	tr	di	—	0.86
MnO	0.08	0.03	Ba	tr.	—	hy	24.30	34.60
MgO	37.25	34.01	Ga	tr	tr	ol	48.40	35.00
CaO	0.65	1.64	In	tr.	—	mt	6.50	6.50
Na_2O	0.07	0.09	Sc	tr.	—	cm	0.15	0.15
K_2O	0.40	0.11	Yt	tr.	—	hm	—	0.80
P_2O_5	0.04	0.04	La	tr.	—	il	—	0.30
H_2O+	13.61	11.09	Zr	tr.	—	pr	0.36	0.72
H_2O-	0.66	1.30	Sn	tr.	—			
CO_2	tr.	—	Pb	tr.	—			
S	0.18	0.34	V	15	—			
Cr_2O_3	0.22	0.17	Cr	1500	1000			
NiO_2	0.22	—	Mo	tr.	—			
	100.06	100.48	Co	65	45			
Less O≡S	0.07	0.09	Ni	1500	500			
Total	99.99	100.39	F	—	—			
Sp.Gr.	2.75	3.11						

I. Olivine-bearing "bastite"-serpentinite requoted from table 4. Analyst, G. H. Francis.

II. Serpentinite with chlorite-tremolite-ore pods, near contact with wall rock, Sgor Gaoithe, Glen Urquhart. Harker Collection no. 76,110. Analyst G. H. Francis.

(a) Chemical analyses.

(b) Spectrographic determination of minor elements in the analyses (parts per milllion): 'tr' means present but below the limits of quantitative determination. Spectrography, Dr. S. R. Nockolds.

(c) C.I.P.W. norms of the two analyses.

Late veins.—Certain late-stage veins have cut the serpentinite. Their time-relation to one another is shown in slides where they intersect. The first group comprises cross-fiber chrysotile and chalcedony veins. In some cases (no. 76.279) chalcedony has been found occupying the center of chrysotile veins, and cutting across them. In others chrysotile cuts chalcedony. Chrysotile veins also cut one another. They all seem broadly contemporary. This group of veins cuts mesh serpentinites, hydrothermally altered rocks, and antigorite rocks. That chrysotile veins could traverse antigoritic rock was doubted by Selfridge, who did not find an example of this relationship in the rocks he studied.

Locally carbonate veins cut the chrysotile veins. They are up to 0.5 mm across and contain magnesite and calcite. The sequence of events in the serpentinite mass is given in table 7.

TABLE 7

Time Sequence in the Serpentinite Mass

Stage	Product	Evidence of relative age
1. Intrusion	enstatite-olivinite	
2. Autometasomatism	"bastite"-serpentinite	Corroded olivines in mesh cores, corroded enstatites in "bastites."
3. Metasomatic injection	marginal modifications, internal zoned bodies	Talc, chlorite, actinolite, anthophyllite, etc., cut across mesh serpentine of stage 2.
4. Antigoritization	Antigorite-serpentinite	Antigorite cuts across stages 2 and 3.
5. Late veining (a)	Chrysotile and chalcedony	Chrysotile and chalcedony roughly contemporary. Chrysotile cuts across stages 2, 3, 4.
6. Late veining (b)	Carbonate veins	Carbonate veins cut chrysotile veins of stage 5.

ACKNOWLEDGMENTS

This work forms part of a thesis on the rocks of Glen Urquhart submitted for the degree of Ph.D. at Cambridge University. I am indebted to Professor C. E. Tilley for advice during the course of the work, to Dr. Hatten S. Yoder, Jr., for the X-ray spectrometer charts, to Dr. S. R. Nockolds for the trace element determinations, to Dr. J. Zussman for X-ray investigation of antigorite and alpha serpentine, and to him and Dr. J. F. G. Wilkinson for useful discussion of the work. Maintenance grants by the Ministry of Education and the Department of Scientific and Industrial Research are gratefully acknowledged.

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CONCENTRATION OF BRINES AND DEPOSITION OF SALTS FROM SEA WATER UNDER FRIGID CONDITIONS*

THOMAS G. THOMPSON and KURT H. NELSON

ABSTRACT. The purpose of this paper is to present evidence that the origin of some salt deposits may have occurred from the concentration of sea water under frigid conditions rather than by evaporation. The order in which salts deposit from brines subjected to such conditions differs from the order in which salts deposit by evaporation. Concentrated brines result from the freezing of sea water from which small quantities of calcium carbonate precipitate. On cooling, sodium sulfate decahydrate is deposited from the brines, followed by the depositions of the sodium chloride dihydrate, potassium chloride, and magnesium chloride. Carnalite can form only as the result of secondary reactions. The embayment and bar theory of Bischof and Ochsenius is applied to explain the deposition of salts by frigid concentration from sea water and also to explain the formation of some sulfate lakes.

INTRODUCTION

An extensive literature exists concerning the evaporation of sea water and the order and nature of the deposition of various salts. The earlier literature is presented and discussed in some detail by Grabau (1920). Summaries of the present knowledge concerning the deposition of oceanic salts by the evaporation of sea water have been given by Clarke (1924) and more recently by Phillips (1947). In explaining the formation of salt deposits, it is generally postulated that all such deposits result from the evaporation of brine, that the ultimate source of such brine was sea water, and that evaporation and formation of salt deposits must necessarily take place in arid or semi-arid regions.

Many salt deposits are of considerable thickness, and to account for such deposits investigators have suggested that great quantities of brine were concentrated by evaporation in deep valleys. Bischof (1864) postulated that accumulation of brines by evaporation would occur in deep embayments separated from the sea by a bar. Ochsenius (1877) further amplified and developed the embayment and bar theory, which is now generally applied to explain the formation of deposits of salts of marine origin. The theory postulates a deep embayment of the ocean, connected to the sea by a shallow and narrow entrance. Climatic conditions subject the waters of the embayment to rapid evaporation. The inflow of water from the surrounding land area is very limited, and the loss of water by evaporation is replaced by the inflow of fresh sea water over the shallow threshold. Due to the evaporation the densities of the surface waters are increased and the concentrated waters sink. In the process of time, a highly saline brine results in the embayment waters below the depth of the threshold. Eventually the shallow channel ceases to exist, and a highly saline, landlocked body of water forms. Evaporation continues and the various salts begin to crystallize, resulting in a thick bed of salt deposits, the thickness of which is a function of the original depth

* Contribution no. 191 from the Department of Oceanography, University of Washington, Seattle, Washington.

of the embayment and the concentration of the brine at the time the water body became landlocked.

Usiglio (1849a and b) has shown that salts formed by the evaporation of sea water are deposited in a definitive order. Traces of ferric oxide were first precipitated together with calcium carbonate when about half of the water had evaporated from the original volume. After 80 percent of the water had evaporated calcium sulfate dihydrate crystallized and continued to form in decreasing amounts, until only 2 percent of the original water remained. Sodium chloride began to separate in quantity after 90 percent of the water had evaporated, and as evaporation continued, increasing amounts of magnesium chloride were associated with it. Other investigators showed later that numerous complex minerals would crystallize from the mother liquors. It has been demonstrated by later investigators that, due to varying conditions of formation, the results of leaching, resolution and reprecipitation of the many double salts, deposition does not always occur in the manner shown by Usiglio and others.

In most of the literature explaining or attempting to account for salt deposits, the process that may take place as the result of freezing of brines is neglected. However, many authors mention the changes in the solubility of the salts that may occur with temperature variation and the possible influence on the nature of the deposits.

Recent investigations in the authors' laboratory (Nelson, 1953; Nelson and Thompson, 1954; Thompson and Nelson, 1954) dealing with the desalting of sea water by freezing and with the deposition of salts in the cold, concentrated brines formed by frigid concentration indicate that the embayment theory of Bischof and Ochsenius could well be applied to regions that had once experienced decided frigid conditions and thus give a more satisfactory explanation of some salt deposits as well as explain the possible origin of certain sulfate lakes.

TEMPERATURES OF MAXIMUM DENSITIES OF FRESH WATER AND SEA WATER

The processes occurring during the cooling and freezing of sea water differ from those of fresh water (Thompson, 1932). Since the temperature of maximum density of pure water is 3.98°C., cooling water below this temperature results in a decrease in the density of the water; the colder, less dense water floats over the denser, warmer water with the eventual formation of ice when the freezing point is reached. When salts are added to fresh water the temperature of maximum density, as well as the freezing point of the solution, is lowered. Thus for sea water with a salinity of 24.70‰ (chlorinity, 13.67‰) the freezing point and the temperature of maximum density are identical, -1.33°C. For each increase of one part per thousand in salinity, the temperature of maximum density is lowered 0.215°C., while the freezing point is decreased only 0.054°C. For sea waters of average salinities the temperatures of maximum density are below the freezing points. Thus as sea water is cooled at the surface there is a continual sinking of the denser water. With sufficient lowering of the temperature, crystals of ice will form which further increase the density of the sea water immediately adjacent to the ice. This water sinks, being replaced by less dense water.

SALTS RETAINED IN ICES FROM SEA WATER AND CONDITIONS RESULTING FROM MELTING OF THE ICES

Malmgren (1923) reported that the salt content of ice produced under natural conditions depends upon the rate of freezing and that the concentration of salts decreased with increasing depth below the surface of the ice. He also noted that the salinity of new ice increased as the temperature decreased.

Thompson and Nelson (1954) froze 1200 ml sea water (salinity 32.5‰) in a paraffined cardboard tube, 6.5 x 45 cm high and sealed at one end with a rubber stopper. Freezing was promoted from the surface downward by insulating the sides of the tube. The experiments were performed at four different temperatures. When thermal equilibrium was reached, the stopper was removed and any remaining brine was permitted to drain from the ice. The ice was then cut into a number of disks each having a thickness of 1 cm. Each disk was melted, and the chlorosity[1] determined for the resulting solu-

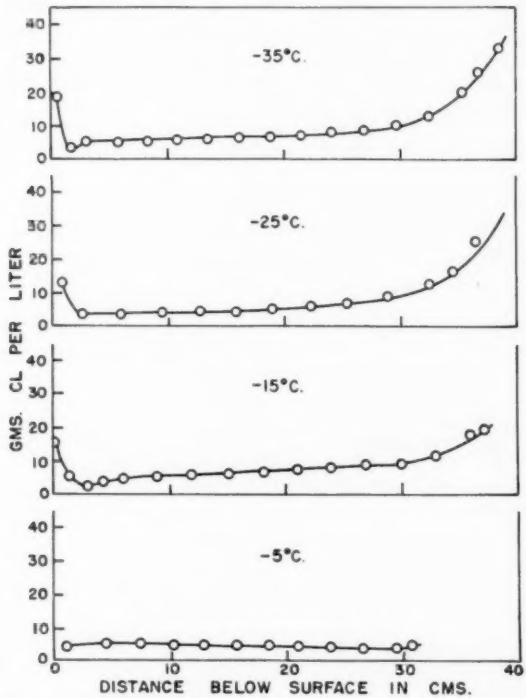

Fig. 1. Concentrations of chlorides retained by ice formed at various depths and temperatures under laboratory conditions. The high concentration at the surface is caused by entrapped sea water as ice first formed.

[1] When the chlorinity, Cl ‰, of a sample of sea water is multiplied by the specific gravity of the water at 20°C., the value obtained is known as the chlorosity and is represented by the symbol, Cl_0 (Helland-Hansen and others, 1948).

tions. The results obtained from ice at four different temperatures are illustrated in figure 1.

The upward slopes of the curves, indicating a greater retention of salts by the ice as the thickness of the ice increased, were due to contact with concentrated brines. This situation would not occur under the natural conditions described by Malmgren.

In another series of experiments, 18 liters of sea water were placed in glass cylinders having diameters of 20 cm and heights of 60 cm. The water in the cylinders was subjected to temperatures of -5°, -15° and -45°C. When thermal equilibrium had been attained, the cylinders were removed from the freezers and the ice allowed to melt at room temperature without the removal of the residual brines at the bottom of the cylinders. When the melting of the ice was complete, samples of water were pipetted from the surface and then at 6-cm intervals. At about 10 cm from the bottom, samples were pipetted at 3-cm intervals. The chlorosity of the samples was determined, and the results obtained are illustrated in figure 2. Convection currents tended to occur during the melting of the ice, which caused slight increases in the salt content of the upper layers. The data, however, demonstrated that about 80 percent of the salt content of the original waters had been concentrated in 20 percent of the original volume.

BRINES AND SALTS FORMED BY FRIGID CONCENTRATION OF SEA WATER

The sea water used in these studies were collected in 20- and 50-liter carboys about 100 miles off the coast of the State of Washington at 47°52.5′ N latitude and 126°17.0′ W longitude. The sea water was filtered through a sintered glass filter of F porosity. The water had a chlorinity of 18.01‰, equivalent to a salinity of 32.54‰.

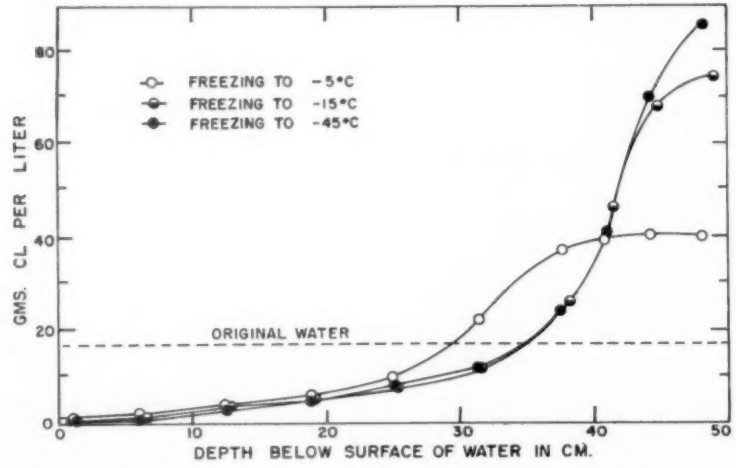

Fig. 2. Chlorosity of the waters and brines resulting from the melting of ice in situ, which had been formed at -5°C., -15°C. and -45°C.

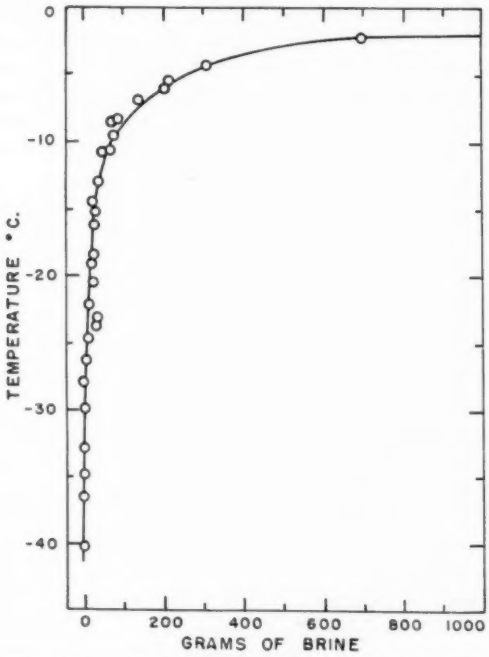

Fig. 3. Grams of brine in equilibrium with ice at various temperatures per kilogram of sea water.

Different aliquots, varying from 1 to 8 liters, were taken from the large volume of sea water and subjected to different temperatures from –2.20°C. to –43.15°C. The aliquots were brought to thermal equilibrium at various temperatures, and the unfrozen brines were drained from the ice, as well as any of the salts which had deposited. The weight and the densities of the brines were determined. Figure 3 shows the grams of unfrozen brine remaining after 1 kilogram of sea water had been subjected to freezing conditions at the various temperatures. Figure 4 gives the densities of the brines.

The various brines were analyzed for the major constituents of sea water. The results of the analyses were calculated as grams of constituent per kilogram of the respective brines, and the data obtained are illustrated in figures 5 and 6.

Precipitation of calcium carbonate.—It was observed that when temperatures of the separated brines increased precipitation of small amounts of calcium carbonate occurred. Generally, the time interval between the separation of the brine and the point of precipitation of calcium carbonate was shortened as the temperature decreased and the salinity of the brine increased. Thus, for brines with temperatures somewhat below the freezing point of the original sea water, a period of several days at room temperature was required before precipitation became noticeable. This time interval was de-

creased to several hours when the temperatures of the brines were slightly above –22.9°C. The brines that had been concentrated between –22.9° and –36.0°C. showed a precipitate in time periods that varied from a few hours to less than an hour after the removal of the brine from the ice. Precipitation of calcium carbonate occurred almost immediately after separation of the brines from salts and ice when the brines had been concentrated below –36.0°C.

Several factors are operative that may cause the precipitation: (a) The solubility of a gas increases with decrease in temperature but decreases as the concentration of electrolytes increases. Thus in the cold concentrated brines the carbon dioxide-water-carbonic acid system is so affected that free carbon dioxide is liberated from solution, the effect of the concentrated electrolytes being more effective than decrease in temperature. This removal of free carbonic acid affects the bicarbonate-carbonate system, as carbon dioxide is no longer present to favor the formation of the more soluble calcium bicarbonate, thus small quantities of calcium carbonate precipitate. (b) As the brines are concentrated, the concentrations of the calcium and carbonate ions are increased to the point where the solubility product of calcium carbonate is exceeded and precipitation results. The detailed mechanisms of this process need further quantitative investigation. The great bulk, however, of calcium

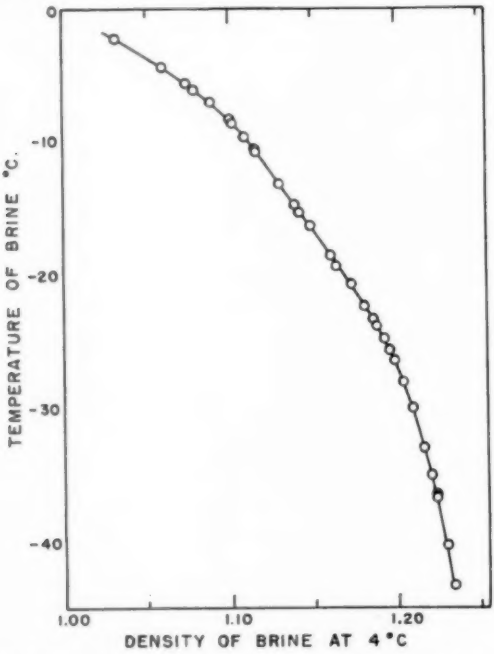

Fig. 4. Densities of brines, measured at 4°C., in equilibrium with ice at various temperatures.

ions remain in solution, and the concentration of these ions increases with the concentration of the brine as shown in figure 5.

Formation of sodium sulfate decahydrate (mirabilite).—The concentration of the sulfate ions increased as the brines were concentrated by decreases in temperature until –8.2°C., when crystals of sodium sulfate decahydrate formed. The deposition of these crystals produced a decided decrease in the sulfate concentrations of the brines as the temperature was further lowered, as indicated in figure 5, and only trace amounts were present at –22°C. Because the sodium ions are in relatively far greater concentrations in the brines than the sulfate ions, there is only a slight noticeable effect indicated by the curve illustrating the sodium ion concentration.

Formation of sodium chloride dihydrate.—At –22.9°C. quantities of sodium chloride dihydrate crystallized from solution, reducing decidedly the concentration of sodium ions in the brine. With further lowering of the temperatures, with the resulting concentration of the brine, the dihydrate continued to crystallize until most of the sodium had been removed from solution. The removal of water by the formation of the dihydrate aided in the further concentration of the brine, and this is indicated by the great increase in the concentration of calcium, magnesium, and potassium ions at temperatures below –22.9°C.

When crystals of the dihydrate are brought to a temperature of about 0°C., the salt loses its water of crystallization. Pure sodium chloride results with the water liberated from the crystals forming a supernatant liquor saturated with sodium chloride which also contains most of the other ions carried down as impurities when the dihydrate precipitated.

Precipitation of potassium and magnesium salts.—The concentration of potassium and magnesium ions increased with decrease in temperature to –36°C. At this temperature the dodecahydrate of magnesium chloride forms together with potassium chloride (sylvite). Below –36°C. there is a marked decrease in the concentration of both potassium and magnesium ions. In the system, potassium chloride, water, and magnesium chloride, carnallite forms only from solutions rich in magnesium chloride and above a temperature of –21°C.

Concentration of calcium ions.—The calcium concentration of the brines increased with decrease in temperature. From the initial freezing point of the original sea water to –22.9° there was a gradual increase in the calcium content of the brine as ice and sodium sulfate decahydrate formed. Between –22.9° and –36°C. the formation of the dihydrate of sodium chloride further concentrated the brine, producing a fourfold increase in the calcium content. As the dodecahydrate of magnesium chloride below –36° crystallized, there was again a considerable increase in the calcium content.

The temperatures at which the various salts formed were obtained by thermal analysis. An inflection point noted at –54°C. indicated the complete solidification of the remaining brine consisting largely of calcium chloride.

Concentration of chloride ions.—Figure 6 illustrates the concentration of chloride in the brines forming at the several temperatures. The curve is analogous to that shown in figure 4 for the densities of the brine but tends

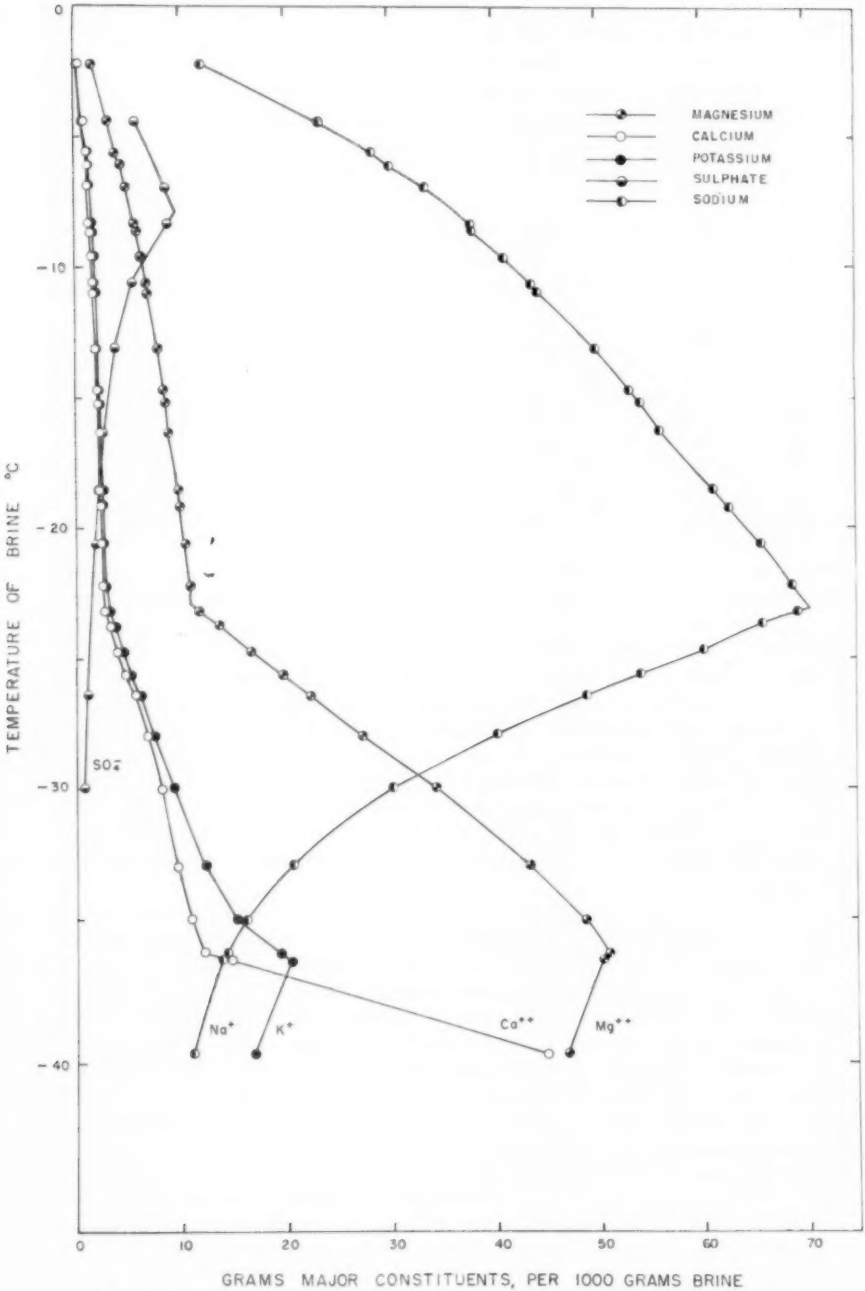

Fig. 5. Concentrations of sulfate, sodium, potassium, magnesium and calcium ions of brines in equilibrium with ice or ice and crystallized salts at various temperatures. The concentrations are expressed as grams of constituent per kilogram of residual brine.

to flatten below –22.4°C. as the salts precipitate. The removal of water, as water of crystallization, counteracts the removal of chloride ions by salt formation, thus giving the characteristics shown by the curve. Of the three major anions in sea water, chlorides, sulfates, and carbonates, the chloride ions are the only ones remaining at lower temperatures. In the present work no attempt was made to study the formation of bromides or borates, but it may be assumed that these substances would be primarily concentrated in the residual brines rich in magnesium, potassium, and calcium.

APPLICATION OF THE EMBAYMENT THEORY OF OCHSENIUS TO FRIGID REGIONS

In applying the embayment and bar theory to frigid regions, there would be a water exchange between the waters at or near the surface of the deep embayment with the waters of the adjacent ocean by flow over the bar or threshold. Under frigid conditions ice would form in the embayment, and the cold, more concentrated sea water would tend to sink toward the bottom of the embayment. With the melting of ice under summer conditions, the fresh and brackish waters formed by the melting of the ice would flow seaward as surface water over the bar, while a counter current of sea water would flow over the deeper portion of the bar into the embayment. This flow of water would be caused by the marked salinity gradient existing between the surface waters of the embayment and the sea water of the adjacent ocean. An ebbing tide would accentuate the outward surface flow, while the flood tide would increase the inward subsurface flow over the bottom of the bar. The effect of diffusion and vertical mixing in the subsurface waters of increased salinity in the embayment would be very minute.[2] With continual repetition of these seasonal phenomena over a period of time a very concentrated brine would eventually accumulate in the embayment below the depth of the bar. Because of the marked differences in density, vertical mixing would occur only to a small extent at the immediate interface of the fresh water and the saline water. In the process of time, a concentrated cold brine would result from which relatively small quantities of calcium carbonate would precipitate. This deposit would be followed by deposition of Glauber's salt or mirabilite. Excessively cold seasons would tend to produce colder brines in the depths of the embayment, which would be unaffected, because of density, by a period of less rigorous cold. Eventually the brine would reach a temperature and concentration which would favor the precipitation of the dihydrate of sodium chloride, and deposits of this salt would build up over the mirabilite. Before the temperature of crystallization of sodium chloride was reached, most of the sulfate would have been removed by precipitation from the brine. The thickness of salts depositing by frigid concentration of the water would be a function of the depth of the embayment, the volume and concentration of the brine, and the temperature. As more and

[2] Smith and Thompson (1927) in their studies of the flow of sea water in the Lake Washington Ship Canal demonstrated conditions that could occur in a freshwater system subjected to inward flow of sea water. They found that sea water would be stored in the bottom of the canal and lake system with relatively little vertical mixing and diffusion. The differences in densities they observed were very much less than the density differences that would occur in embayments subjected to freezing and thawing conditions.

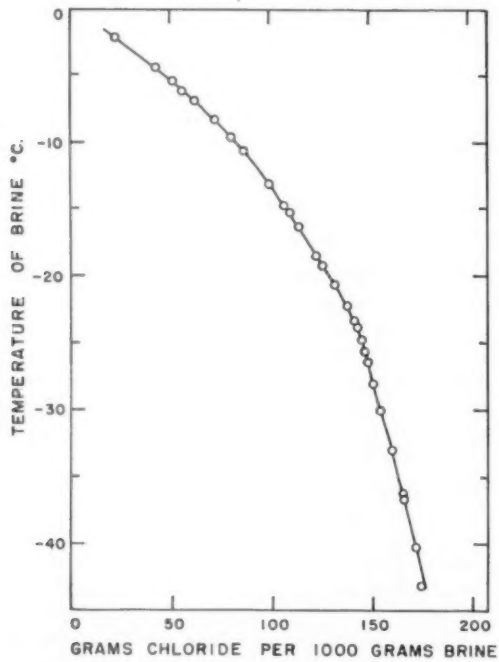

Fig. 6. Concentrations of halides, measured as chlorides, in brines in equilibrium with ice and crystallized salts at various temperatures.

more of the sodium chloride separated from solution, the brine would not only increase in density but also become considerably richer in the chlorides of magnesium, potassium, and calcium. From this brine, potassium chloride (sylvite) would precipitate together with the dodecahydrate of magnesium chloride.

With the increase in height of the bar connecting the embayment with the sea, the original embayment would become landlocked. Changes in climatic conditions over geologic time due to increases in temperature would cause alterations in the system. As the temperature of the supernatant brine increased, any dodecahydrate of magnesium chloride which had deposited would tend to dissolve in its own water of crystallization and mingle with the brine. Depositions of sylvite would not be affected because it is far less soluble. From phase rule considerations, the concentrations of magnesium and potassium are such that deposition of $MgCl_2.KCl.6H_2O$ (carnalite) would begin to deposit at –21°C. from the magnesium-enriched brine.

As the mass of dihydrated sodium chloride reached a temperature approaching 0°C., it would lose its water of crystallization and give rise to a much purer deposit of halite than could be obtained by evaporation; the liberated water of crystallization, in reality a saturated solution of sodium

chloride, would wash from the anhydrous crystals of sodium chloride some of the impurities mechanically retained when the deposit of the dihydrate first formed. Such deposits would be characterized by the presence of very small quantities of calcium and magnesium salts, especially sulfates. Deposits formed by evaporation would have considerably greater quantities of these salts, especially the sulfates.

Mirabilite or saturated solutions of the mineral would tend under proper conditions to react very slowly with calcium carbonate, with the formation of calcium sulfate and sodium carbonate.[3] This is due largely to the common ion effect of the high concentration of the sulfate ions. Conditions existing would depend upon the appearance of calcium sulfate as anhydrite ($CaSO_4$), gypsum ($CaSO_4.2H_2O$), or glauberite ($Na_2SO_4.CaSO_4$). Retained water in the deposits would be a saturated solution of sodium sulfate containing sodium carbonate. As deposits of halite formed, and with the increasing pressure, the solutions of sodium sulfate and carbonate would be forced upward into the strata of halite. This process thus gives an explanation of the occurrence of sodium carbonate and sulfate in some salt deposits. The presence of such salts could hardly be accounted for by a process of concentration depending solely on evaporation.

ORIGIN OF SULFATE LAKES

An explanation of the formation of many sulfate lakes, once lagoons or embayments of the sea, appears to be more logical by assuming concentration of brines, derived originally from sea water, by frigid conditions rather than by any conditions that could be obtained solely by evaporation. Such lakes at present are characterized by a high concentration of sodium sulfate (from which crystals of sodium sulfate precipitate during the winter months), high alkalinity due to the presence of sodium carbonate, relatively high concentrations of sodium chloride, and only small amounts of magnesium and calcium salts. The sea water from which the sulfate lake waters were derived was concentrated in the manner outlined above with the resultant precipitation of calcium carbonate, the partial action of saturated solutions of sodium sulfate on the calcium carbonate to form sodium carbonate, and the formation of mirabilite and halite. With changing conditions over geological time, the residual brines were removed by continual leaching or drainage from the surface.

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EXPERIMENTAL DATA ON THE P_{CO_2}-T CURVE FOR THE REACTION: CALCITE + QUARTZ ⇄ WOLLASTONITE + CARBON DIOXIDE*

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ABSTRACT. The univariant P_{CO_2}-T curve for the reaction calcite + quartz ⇄ wollastonite + CO_2 has been determined experimentally. This experimental curve has been compared to those curves for the same reaction that have been determined by calculations.

The geologic significance of the reaction is discussed, and it appears that, at pressures of less than 40,000 lbs./in.^{2} in the Earth's crust, the P_{CO_2}-T curve for the formation of wollastonite + CO_2 from calcite + quartz lies at lower temperatures than that for the formation of periclase + calcite + CO_2 from dolomite.

INTRODUCTION

As part of an investigation of the stability of the phases in the CaO—MgO—SiO_2—CO_2 system with excess CO_2 the reaction $CaCO_3 + SiO_2 \rightleftarrows CaSiO_3 + CO_2$ has been studied. The common occurrence of siliceous impurities in limestones, which are thus a potential or actual source of wollastonite, renders this reaction extremely important from a geologic standpoint. Goldschmidt (1912) realized this over forty years ago when he published the univariant P-T curve for the reaction as deduced from the Nernst approximation formula. Since then various other attempts have been made to determine points on the P-T curve both by experiment, e.g. Kröger and Illner (1936) and by calculation (see Danielsson, 1950).

The univariant reaction involves the three components CaO, SiO_2 and CO_2 and a discussion of the reaction and its effect on compositions, represented by different points along the $CaCO_3$-SiO_2 join, has been presented by Bowen (1940).

APPARATUS

All the experimental work was carried out using cold-seal pressure vessels designed by Tuttle (1949). The apparatus as a whole has been described in detail in connection with work done in the CaO—MgO—CO_2 system (Harker and Tuttle, 1955), so that only a brief resumé is necessary here. A hydraulic jack pump and an experimental pressure unit are the two main components of the apparatus. The pump is used to compress the CO_2 in the pressure unit which consists of a valve, a bourdon pressure gauge, and a cold-seal pressure vessel over which a movable furnace is mounted. The valve of the pressure unit is placed between the pump on the one hand and the pressure vessel and gauge on the other. When the desired pressure of CO_2 in the pressure unit has been reached by the operation of the pump, this valve is closed and the furnace is lowered over the pressure vessel. The temperature of the furnace is controlled to ± 5°C. by a galvanometer-type controller, and the pressure is maintained at the desired amount by bleeding out CO_2 as necessary through the valve as the temperature of the pressure vessel is raised. The measured pressures are believed to be accurate to ± 3 percent. The rate at

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which the pressure vessel is heated can be controlled by adjusting the temperature of the furnace when this is lowered initially onto the pressure vessel.

Some modification of this apparatus was necessary for the work carried out at the higher pressures. It was often difficult and sometimes impossible to contain the CO_2, without some leakage for a sufficient length of time for appreciable reaction to take place. To overcome this difficulty, a second pressure vessel and furnace were connected to the original pressure unit as shown in figure 1. No samples were placed in this second pressure vessel but it contained a relatively large volume of CO_2 which could be heated as necessary. A micro-switch was attached to the dial of the pressure gauge and was operated by the dial pointer. When the pressure dropped because of a leak in the system the furnace over the second pressure vessel was automatically switched on until, by the increase of pressure of the CO_2 in this second vessel, the pressure in the unit as a whole was maintained. It was found that this arrangement was very satisfactory even though of course it could not compensate for severe leaks over long periods of time. (The limit of compensation was reached when the second pressure vessel had attained the maximum safe temperature at the particular pressure of the experiment.)

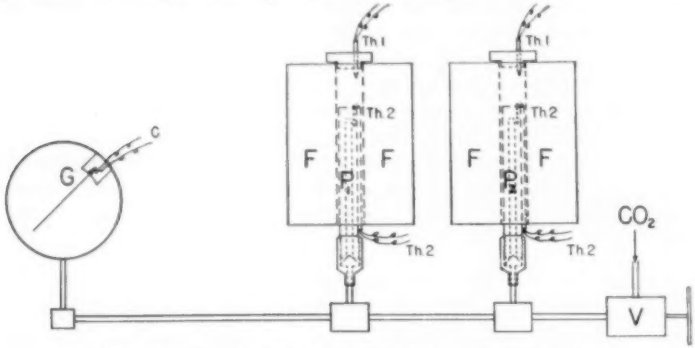

Fig. 1. Scale diagram of apparatus (in part schematic)
G = Gauge (diameter = 6″)
F = Furnace
P_1 and P_2 = First and second pressure vessels
V = Valve
C = Pressure control switch
Th. 1 = Thermocouple for controlling furnace temperature
Th. 2 = Thermocouple for measuring temperature of sample.

STARTING MATERIALS

In each experiment, samples of calcium carbonate + silica and of wollastonite were loaded into the pressure vessel.

In natural rocks the calcium carbonate and silica are usually in the form of calcite and quartz. In these experiments, calcite and quartz were normally used and found to be no less reactive under the right conditions than other starting materials, e.g. aragonite, silica glass, and cristobalite. The calcite was the analytical reagent of the Fisher Scientific Company, and the quartz was

a pure variety from a vein at Lake Toxaway, North Carolina, having less than 0.05 percent of residue after evaporation with HF + H_2SO_4 and subsequent ignition. The wollastonite which was most successful as starting material for the runs was made synthetically by reacting a mixture of the aforementioned calcite and quartz at 800°C. and 30,000 lbs./in.^{2} of CO_2. At this temperature and pressure the reaction could be made to go almost to completion overnight. The synthetic wollastonite so produced was treated with dilute HCl to remove the traces of calcite which had not reacted, and the remaining wollastonite was thus always accompanied by a small amount of excess quartz. A natural wollastonite was used in a few of the runs but was not so reactive as the synthetic material.

EXPERIMENTAL PROCEDURE

During runs made on the low temperature side of the P-T curve calcite and quartz are stable together and may recrystallize in equilibrium with one another. On the other hand, the wollastonite tends to react with the excess CO_2 to produce calcite and quartz. During runs made on the high temperature side of the P-T curve the wollastonite may recrystallize in stable equilibrium with CO_2, while the calcite and quartz tend to react with each other to produce wollastonite and CO_2.

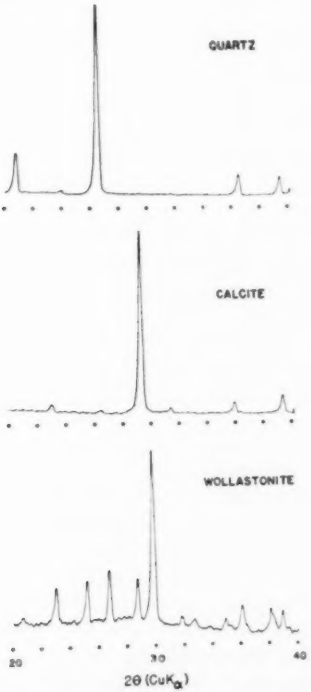

Fig. 2. X-ray powder diffraction patterns for quartz, calcite, and wollastonite.

The solubilities of the solid phases in the CO_2 at elevated temperatures and pressures are unknown but are presumed to be very small. The samples were not depleted during the runs, and there was no evidence of reprecipitation of material outside the crucibles containing the samples.

The products of the runs could be identified with the aid of a petrographic microscope and an X-ray spectrometer. The X-ray patterns for calcite, quartz, and wollastonite are shown in figure 2.

In practice, the chief difficulty in recognizing the stable assemblages arose from the slow rate of the reactions. Apart from a general sluggishness, the reactions go more slowly in the immediate vicinity of the P-T curve than at pressures and temperatures a little further removed from it. It is fortunate, however, that the reaction which goes with falling temperature and less readily, i.e. Wollastonite + CO_2 ⟶ Calcite + Quartz, is more easily detected than the reverse reaction which goes with rising temperature. This is because the development of calcite in very small quantities can readily be detected both optically, because of the high birefringence, and with the X-ray spectrometer, because of the very strong {211} peak, before the presence of equally small amounts of wollastonite are evident.

At pressures greater than 15,000 lbs./in.^{2} it would be possible to determine the P-T curve without the aid of any flux to facilitate reaction, and at the beginning of this investigation no flux was used. However, in order to obtain any reliable data on the location of the P-T curve at lower pressures it was desirable to increase the rates of reaction. Experiments using different catalysts, i.e. $CaCl_2$, CaF_2, NaF, Na_2WO_4 and $PtCl_2$, had been carried out by Kröger and Illner (1939), but in the present apparatus the presence of as little as 0.02 cc of water was found to be extremely effective in increasing the rates of reaction. Thereafter this amount was added to the majority of the powdered samples before they were placed in the pressure vessels, for runs at both higher and lower pressures. This small amount of water produced no hydrous phases, and presumably the temperature was consistently too high for their formation. However, the partial pressure of CO_2 with some water present is, of course, somewhat less than the total hydrostatic pressure of CO_2 + H_2O which is measured on the gauge. It was estimated that the partial pressure of H_2O derived from the addition of 0.02 cc. of water was less than 1/1000 of the total pressure of the P-T range under investigation. It was not surprising, therefore, that the use of a very small amount of water as a catalyst did not displace the P-T curve from its position as deduced from the earlier "dry" runs. The system was still univariant within the limits of accuracy of measurement, and it was considered unnecessary to apply any corrections either to estimate the actual pressure of CO_2 from the total pressure or to allow for the fact that the pressure of CO_2 was very slightly different from the hydrostatic pressure on the solid phases in the "wet" runs.

The majority of the successful runs made to determine the P-T curve are listed in table 1 in which the "dry" and the "wet" runs are differentiated. It is evident by comparing the results of a number of runs that reaction takes place more readily in the "wet" than in the "dry" runs. For example, no reaction could be detected between calcite and quartz at 750°C. and 30,000

lbs./in.^{2} in 168 hours, but the reaction forming wollastonite went almost to completion under the same conditions of temperature and pressure in 24 hours after the samples had been moistened. At 800°C. and 30,000 lbs./in.^{2} wollastonite was readily produced overnight, and much of the synthetic wollastonite used as starting material was prepared under these conditions. The reaction was found to go almost to completion if the sample was moistened initially.

Occasionally, a "dry" run would react surprisingly thoroughly, and it is considered most likely that in such cases some moisture must have found its way into the run. For example, more wollastonite was produced at 730°C. and 15,000 lbs./in.^{2} in 240 hours than at 750°C. at the same pressure and in the same length of time.

The increased reactivity induced by the presence of a small quantity of water introduced some practical disadvantage. From several "wet" runs anomalous results were obtained and runs repeated at a particular pressure and temperature and for a particular length of time gave widely different results. It was thought that slight variations in the amount of water added might be the cause of the inconsistencies, but further experiments in which the amount of water used was varied indicated that this was not so. The difficulty was overcome when it was discovered that the inconsistencies arose due to a variation in the rates of initial heating. With a small amount of moisture present reaction was so promoted that it tended to take place in the starting materials during the initial heating of the pressure vessel before it had settled down to run at the required temperature and pressure. During the initial heating the pressure in the pressure vessel was always such that if CO_2 alone were present the P-T conditions would have been on the low temperature side of the P-T curve. Thus there may have been some opportunity for wollastonite to break down to calcite and quartz before the run had settled down to the desired P-T conditions. When these conditions were attained, the starting material, which was loaded into the pressure vessel as wollastonite with a little excess quartz, then contained some calcite. Furthermore, as the temperature of the pressure vessel was raised during the initial heating, the moisture in the sample tended to migrate to the cooler regions of the pressure unit so that the catalyst was gradually removed from the immediate sphere of activity. This was evident from observations at the conclusion of the runs when the products were found to be dry. Thus although the temperature of the sample was being raised, the rate of possible reactions may have decreased and reaction may have taken place more readily during the initial heating than at the higher temperature of the run proper.

In some experiments, at a particular pressure and temperature, wollastonite was found to grow from a calcite + quartz mix while in the same experiment calcite could be seen to have developed from the synthetic wollastonite during the initial heating. In examples such as this it is possible that in the earliest stages of the initial heating the partial pressure of water from the moistened sample was indeed appreciable, so that the CO_2 pressure was correspondingly reduced and some wollastonite was able to develop.

TABLE 1

$$CaCO_3 + SiO_2 \rightleftarrows CaSiO_3 + CO_2$$

Run	Initial Materials		Temp. °C.	Pressure lbs./in.^{2} x 10^3	Time Hrs.	Products	
1	Ct + SiO_2 (glass)	d	700	45	240	Ct + Qtz	
2	Ct + Qtz	d	"	"	"	Ct + Qtz	
3	Ct + Qtz	w	750	"	89	Ct + Qtz	
4	Woll (+ Qtz)	w	"	"	"	Ct + Qtz	
5	Ct + Qtz	w	800	"	16	Ct + Qtz	
6	Woll (+ Qtz)	w	"	"	"	Woll + Qtz + Ct	
7	Ct + Qtz	w	750	40	1/12	Woll (+ Ct + Qtz)	
8	Ct + Qtz	w	"	"	3	Woll + Ct + Qtz	Calcite
9	Ct + Qtz	w	"	"	48	Ct + Qtz (+ Woll)	+
10	Woll (+ Qtz)	w	"	"	1/12	Woll (+ Qtz)	Quartz
11	Woll (+ Qtz)	w	"	"	3	Woll (+ Qtz)	growing
12	Woll (+ Qtz)	w	"	"	48	Ct + Qtz	
13	Ct + Qtz	w	780	"	1/6	Woll (+ Ct + Qtz)	
14	Ct + Qtz	w	"	"	1-1/2	Woll (+ Ct + Qtz)	
15	Ct + Qtz	w	"	"	24	Woll + Ct + Qtz	Calcite
16	Woll (+ Qtz)	w	"	"	1/6	Woll (+ Qtz)	+
17	Woll (+ Qtz)	w	"	"	1-1/2	Woll (+ Ct + Qtz)	Quartz
18	Woll (+ Qtz)	w	"	"	24	Ct + Qtz (+ Woll)	growing
19	Ct + Qtz	w	800	"	1/60	Woll (+ Ct + Qtz)	
20	Ct + Qtz	w	"	"	1/6	Woll	
21	Ct + Qtz	w	"	"	2	Woll	Calcite
22	Ct + Qtz	w	"	"	120	Woll	+
23	Woll (+ Qtz)	w	"	"	1/60	Woll (+ Ct + Qtz)	Quartz
24	Woll (+ Qtz)	w	"	"	1/6	Woll (+ Ct + Qtz)	growing
25	Woll (+ Qtz)	w	"	"	2	Woll (+ Qtz)	
26	Woll (+ Qtz)	w	"	"	120	Woll (+ Qtz)	
27	Ct + Qtz	w	800	38.5	120	Woll	
28	Woll (+ Qtz)	w	"	"	"	Woll (+ Qtz)	
29	Ct + Qtz	w	740	33	42	Ct + Qtz	
30	Woll (+ Qtz)	w	"	"	"	Woll (+ Ct + Qtz)	
31	Ct + Qtz	w	740	32	24	Woll	Calcite
32	Ct + Qtz	w	"	"	96	Woll + Ct + Qtz	+
33	Woll (+ Qtz)	w	"	"	24	Woll (+ Qtz)	Quartz
34	Woll (+ Qtz)	w	"	"	96	Woll + Ct + Qtz	growing
35	Ct + Qtz	w	710	31	288	Ct + Qtz	
36	Woll (+ Qtz)	w	"	"	"	Ct + Qtz	
37	Ct + Qtz	d	600	20	576	Ct + Qtz	
38	Woll (+ Qtz)	d	"	"	"	Woll (+ Ct + Qtz	
39	Ct + SiO_2 (glass)	d	650	"	552	Ct + Qtz	
40	Woll (+ Qtz)	d	"	"	"	Woll (+ Ct + Qtz	Calcite +
41	Ct + Qtz	d	700	"	240	Ct + Qtz	Quartz stable
42	Ct + Qtz	d	"	"	504	Ct + Qtz	Calcite +
43	Woll (+ Qtz)	d	"	"	240	Woll (+ Ct + Qtz)	
44	Woll (+ Qtz)	d	"	"	504	Woll + Ct + Qtz	Quartz
45	Natural Woll.	d	"	"	240	Woll	growing
46	Ct + Qtz	d	750	"	168	Ct + Qtz	
47	Woll (+ Qtz)	d	"	"	"	Woll (+ Qtz)	
48	Ct + Qtz	w	"	"	24	Woll (+ Qtz + Ct)	
49	Woll (+ Qtz)	w	"	"	"	Woll (+ Qtz)	
50	Ct + Qtz	d	800	"	16	Woll (+ Ct + Qtz)	
51	Ct + Qtz	w	"	"	"	Woll	
52	Ct + Qtz	w	640	16	120	Ct + Qtz	
53	Woll (+ Qtz)	w	"	"	"	Woll + Ct + Qtz	
54	Ct + Qtz	w	670	"	44	Ct + Qtz	
55	Woll (+ Qtz)	w	"	"	"	Woll + Ct + Qtz	

TABLE 1 (Continued)

Run	Initial Materials		Temp. °C.	Pressure lbs./in.^{2} x 10^5	Time Hrs.	Products	
56	Ct + Qtz	d	580	15	576	Ct + Qtz	
57	Woll (+ Qtz)	d	"	"	"	Woll (+ Ct + Qtz)	
58	Ct + Qtz	d	610	"	528	Ct + Qtz	
59	Woll (+ Qtz)	d	"	"	"	Woll (+ Ct + Qtz)	
60	Ct + Qtz	d	640	"	576	Ct + Qtz	
61	Ct + Qtz	d	"	"	960	Ct + Qtz	
62	Woll (+ Qtz)	d	"	"	576	Woll (+ Ct + Qtz)	
63	Woll (+ Qtz)	d	"	"	960	Woll (+ Ct + Qtz)	
64	Ct + Qtz	w	690	"	1/2	Ct + Qtz	
65	Ct + Qtz	w	"	"	24	Woll + Ct + Qtz	
66	Ct + Qtz	w	"	"	96	Woll + Ct + Qtz	Wollastonite growing
67	Woll (+ Qtz)	w	"	"	1/2	Woll + Ct + Qtz	
68	Woll (+ Qtz)	w	"	"	24	Woll (+ Ct + Qtz)	
69	Woll (+ Qtz)	w	"	"	96	Woll (+ Ct + Qtz)	
70	Ct + Qtz	d	700	"	960	Woll + Ct + Qtz	
71	Woll (+ Qtz)	d	"	"	"	Woll (+ Qtz)	
72	Ct + Qtz	d	730	"	240	Woll (+ Qtz)	
73	Ct + Qtz	d	750	"	"	Woll (+ Ct + Qtz)	
74	Woll (+ Qtz)	d	"	"	"	Woll (+ Qtz)	
75	Ct + Qtz	d	750	10	168	Woll + Ct + Qtz	
76	Ct + Qtz	d	725	9.5	96	Woll + Ct + Qtz	
77	Ct + Qtz	w	550	7	216	Ct + Qtz	
78	Woll (+ Qtz)	w	"	"	"	Ct + Qtz	
79	Ct + Qtz	w	590	5	192	Ct + Qtz	
80	Woll (+ Qtz)	w	"	"	"	Ct + Qtz + Woll	
81	Ct + Qtz	w	600	"	1	Ct + Qtz + Woll	
82	Ct + Qtz	w	"	"	20	Ct + Qtz	
83	Ct + Qtz	w	"	"	42	Ct + Qtz	Calcite + Quartz growing
84	Ct + Qtz	w	"	"	92	Ct + Qtz	
85	Woll (+ Qtz)	w	"	"	1	Woll (+ Qtz)	
86	Woll (+ Qtz)	w	"	"	20	Woll (+ Ct + Qtz)	
87	Woll (+ Qtz)	w	"	"	42	Woll + Ct + Qtz	
88	Woll (+ Qtz)	w	"	"	92	Ct + Qtz + Woll	
89	Ct + Qtz	w	620	"	1	Ct + Qtz	
90	Ct + Qtz	w	"	"	18	Ct + Qtz (+ Woll)	
91	Ct + Qtz	w	"	"	44	Ct + Qtz + Woll	
92	Ct + Qtz	w	"	"	92	Woll + Ct + Qtz	Wollastonite growing
93	Woll (+ Qtz)	w	"	"	1	Woll + Ct + Qtz	
94	Woll (+ Qtz)	w	"	"	18	Woll + Ct + Qtz	
95	Woll (+ Qtz)	w	"	"	44	Woll (+ Ct + Qtz)	
96	Woll (+ Qtz)	w	"	"	92	Woll (+ Ct + Qtz)	
97	Ct + Qtz	w	645	"	1/12	Ct + Qtz	
98	Ct + Qtz	w	"	"	43	Ct + Qtz (+ Woll)	
99	Ct + Qtz	w	"	"	86	Woll + Ct + Qtz	Wollastonite growing
100	Woll (+ Qtz)	w	"	"	1/12	Woll + Ct + Qtz	
101	Woll (+ Qtz)	w	"	"	43	Woll + Ct + Qtz	
102	Woll (+ Qtz)	w	"	"	86	Woll (+ Ct + Qtz)	
103	Ct + Qtz	w	660	"	1/2	Ct + Qtz (+ Woll)	
104	Ct + Qtz	w	"	"	18	Ct + Qtz + Woll	Wollastonite growing
105	Woll (+ Qtz)	w	"	"	1/2	Ct + Qtz + Woll	
106	Woll (+ Qtz)	w	"	"	18	Woll (+ Ct + Qtz)	

Legend
Ct = Calcite, Qtz = Quartz, Woll = Wollastonite.
(Ct), (Qtz), (Woll) = a trace of calcite, quartz, wollastonite respectively.
d = "dry" (no water added).
w = "wet" (samples moistened with water).

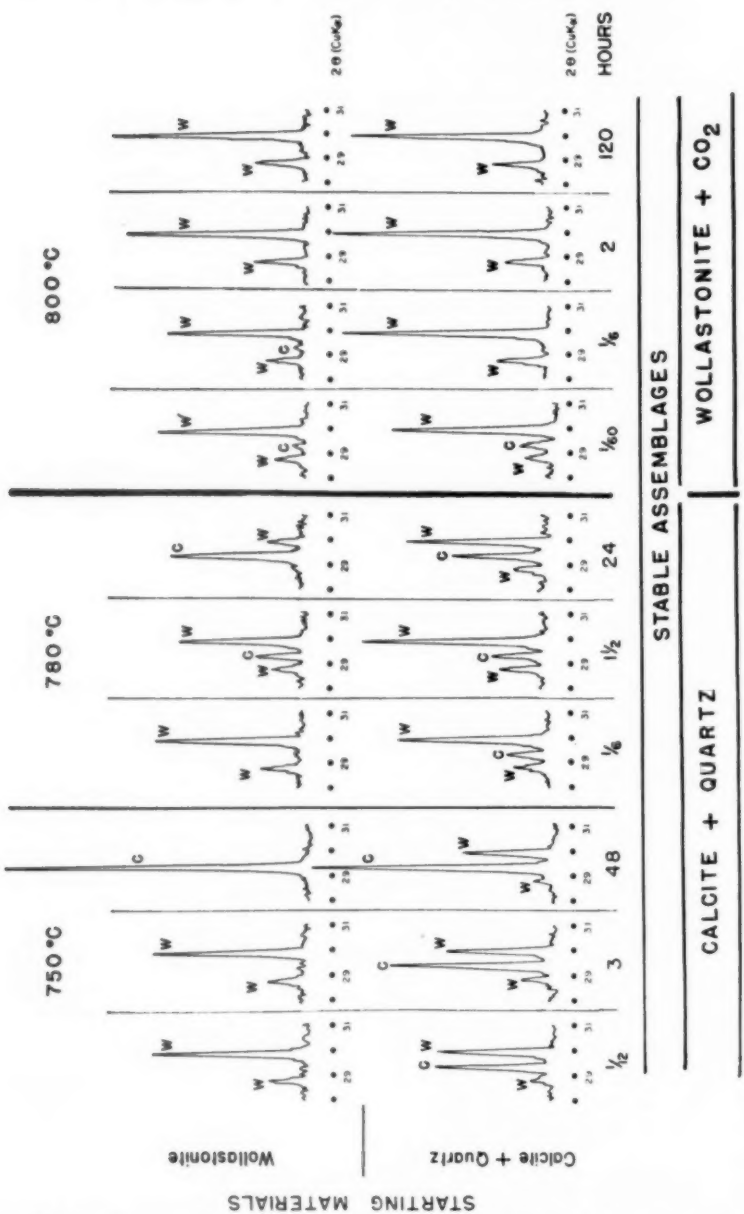

Fig. 3. X-ray powder diffraction patterns (CuKα radiation) for runs made at 40,000 lbs./in.^{2} at different temperatures and for varying lengths of time as indicated. W = Peaks formed by wollastonite; C= Peak formed by calcite.

The nature of the starting materials at the beginning of a run could be determined only by adopting a constant rate of heating and by making a preliminary run in which the pressure vessel was quenched as soon as, or very soon after, the desired P-T conditions of the run proper had been attained. If a constant rate of heating was not always used, then each starting material was able to react to a different extent during the initial heating. In practice the rate of heating consistently used was about 120°C. per minute.

By repeating the runs at one pressure and temperature, but for different lengths of time, it was possible to determine which way the reaction was going under the particular P-T conditions being investigated.

Figure 3 illustrates the X-ray patterns of a series of such runs at 40,000 lbs./in.^{2}. At 750°C. three pairs of runs were made at this pressure for 5 mins., 3 hrs. and 48 hrs. The patterns cover the critical range between 28° and 31° of 2θ (for CuKα radiation) which contains the characteristic peaks of wollastonite, labeled W, and of calcite, labeled C. At this temperature it is clear that calcite (+ quartz, not shown in the X-ray patterns) is increasing at the expense of wollastonite (+ CO_2). The same applies at 780°C., and it must be concluded that at 40,000 lbs./in.^{2} the P-T curve must lie above 780°C. Four pairs of runs were made at 800°C. and 40,000 lbs./in.^{2} and, as the duration of the runs was increased, it can be seen from the patterns that wollastonite developed at the expense of calcite. Only by considering the time factor in this manner could anomalies due to the initial heating be overcome. At the beginning of the runs at 800°C., for example, it appears that some of the wollastonite starting material broke down to calcite while much of the calcite + quartz mixture reacted to produce wollastonite.

A series of runs carried out at 5000 lbs./in.^{2} is illustrated in a similar way in figure 4. At 600°C. there is no doubt that calcite and quartz are stable although a little wollastonite developed initially from the quartz + calcite mix, as seen in the run of one-hour duration. At this pressure and temperature the synthetic wollastonite progressively broke down, as indicated by the increase of the calcite peak relative to the wollastonite peaks. At 620°C., wollastonite grew progressively from the calcite + quartz mix, and that calcite which developed initially from the synthetic wollastonite decreased in amount as the duration of the run was increased.

DISCUSSION OF RESULTS

The P-T curve determined by the experimental runs is shown in figure 5. The position of this P-T curve lies approximately midway between the curve calculated by Goldschmidt (1912), using the Nernst approximation formula, and that determined by Danielsson (1950), using all the recent thermodynamic data available on the phases involved (see fig. 6).

When considering the geologic significance of this P-T curve for the formation of wollastonite + CO_2 from calcite + quartz, it is necessary to bear in mind the various factors which in nature may modify the simplified conditions realized in the laboratory. Complexities may be expected to arise in nature due to the presence of other components, which may enter into the structure of the solid phases, and to the fact that even in a very small volume

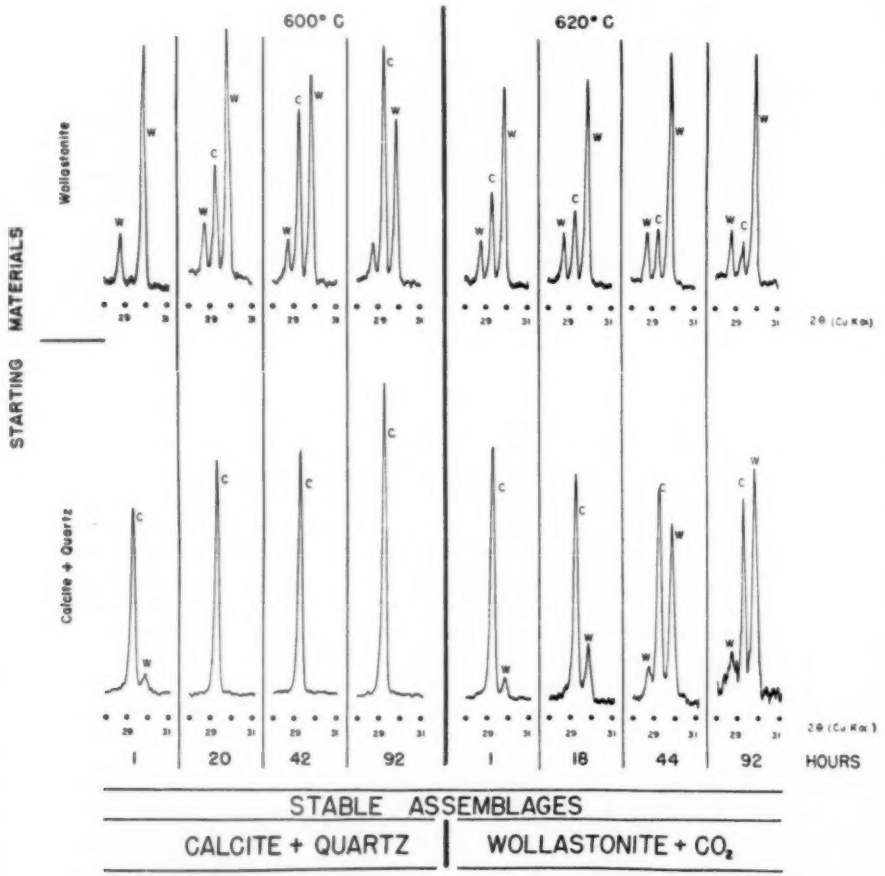

Fig. 4. X-ray powder diffraction patterns (CuKα radiation) for runs made at 5000 lbs./in.^{2} at different temperatures and for varying lengths of time as indicated. W = Peaks formed by wollastonite; C = Peak formed by calcite.

of rock the pressure of CO_2 may vary continuously and differently in different circumstances, and in any event may not be the same as the rock pressure.

Of the additional components most likely to be encountered in the solid phases in natural limestones, MgO and FeO are perhaps the most important. The effect of these on the reaction must remain unknown until further experimental work can be carried out, but it is clear that the addition of such components, even in small amount, if they actually enter the structure of the phases involved, would render the reaction no longer strictly univariant. In this case the apparently stable coexistence of calcite, quartz, and wollastonite (+ CO_2) in a rock (e.g. Pitcher, 1950) would not necessarily indicate that the assemblage represented conditions of univariant equilibrium.

With regard to the pressure of CO_2, it must be borne in mind that if an estimate of the pressure is to be made it may differ somewhat from the rock pressure due to overburden. It could be greater or it could be less and it may increase and/or decrease during the course of the reaction.

It is considered likely, however, that the pressures of CO_2 in the Earth's crust may as a rule be considerable and comparable with the rock pressures. No doubt certain factors tend to reduce the CO_2 pressure, e.g. (1) a dilution of the fluid phase by some other volatile components or (2) the escape of CO_2 through fissures. On the other hand, if the CO_2 pressure is not appreciable then wollastonite would be a common product of regional metamorphism, for there is no reason to suppose that the reaction between quartz and calcite to produce wollastonite cannot take place below 400°C. That there are large quantities of CO_2 available in the Earth's crust is further evidenced by the frequent appearance of carbonate veins in metamorphosed non-carbonate

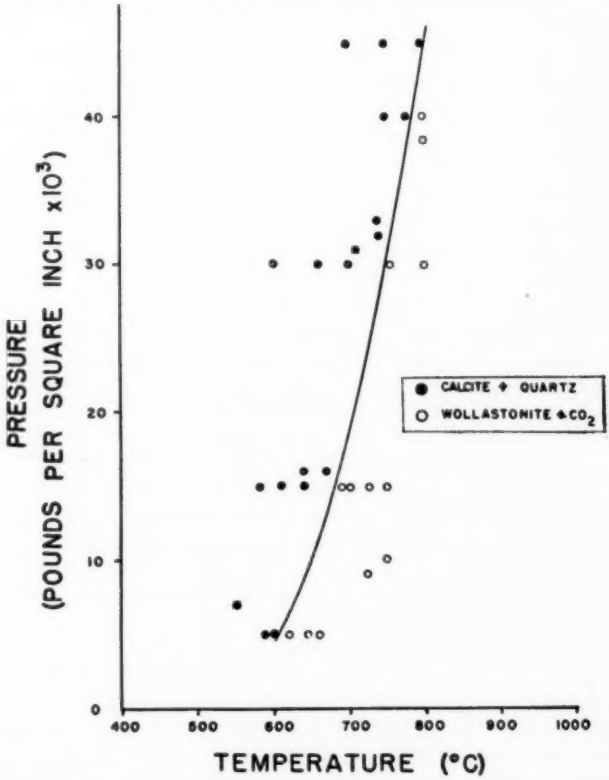

Fig. 5. P_{CO_2}-T curve for the univariant reaction calcite + quartz $\rightleftarrows$ wollastonite + carbon dioxide. The points indicate the pressure-temperature conditions of the runs and the stable phases in the products.

rocks and the relatively high percentage of CO_2 often found in natural gas wells. Furthermore, if the total pressure is appreciably greater than the pressure of CO_2, then it appears that the reaction forming wollastonite goes at a lower temperature for a particular pressure of CO_2 than it would under conditions where the CO_2 pressure is equal to the total pressure on the solid phases (Danielsson, 1950, fig. 4). It may be, of course, as Danielsson pointed out, that a considerable CO_2 pressure may be built up in a siliceous limestone during metamorphism by the formation of a very small amount of wollastonite, invisible even under high magnification, if the rock has very little porosity.

Though it is thought probable that the CO_2 pressure in the carbonate rocks of the Earth's crust usually accounts for an appreciable percentage of the total hydrostatic pressure, it is considered unlikely that the CO_2 pressure ever appreciably exceeds the rock pressure. Experience with oil wells shows that it is difficult to maintain fluid pressures, at least artificially, greater than the rock pressures.

In the geologic applicability of phase equilibria in the system CaO—MgO—SiO_2—CO_2 Bowen (1940) emphasized the role of water in the earlier stages of metamorphism with the consequent formation of tremolite (and of talc, see Tilley, 1948). In the "dry" system diopside may be expected to develop in magnesium-bearing siliceous limestones as a result of decarbonation at lower temperatures than those at which calcite and quartz become unstable together because diopside-calcite-quartz assemblages are not uncommon in the amphibolite facies (Turner, 1948).

The relative temperatures of formation of forsterite and wollastonite by decarbonation reactions at any particular pressure are more uncertain, as it is unlikely that either quartz + calcite + forsterite + CO_2 or wollastonite + forsterite + CO_2 would constitute stable assemblages over any divariant range of P-T conditions. In other words, the development of wollastonite and forsterite by decarbonation reactions could not take place in a rock of one composition. In Bowen's decarbonation series forsterite comes in before diopside but its formation involves the dehydration of tremolite. The greater abundance of diopside over forsterite (or serpentine derived from forsterite) in dolomitic aureoles in the field suggests that diopside appears before forsterite with rising temperature (J. Gilluly, personal communication), and in parts of New England it is thought that diopside is characteristic of a lower grade of metamorphism than forsterite (J. B. Thompson, personal communication).

As was previously anticipated (Harker and Tuttle, 1955), the P-T curve for the formation of wollastonite + CO_2 from calcite + quartz (hereafter called the wollastonite curve) does not cross the P-T curve for the breakdown of dolomite to calcite + periclase + CO_2 (hereafter called the dolomite curve) within the range of pressure and temperature of these experiments. From petrographic evidence, Bowen (1940) considered it likely that whereas at higher pressures the wollastonite curve probably lay at lower temperatures than the dolomite curve, the positions of the curves might well be reversed at lower pressures. The possibility of the two curves crossing at pressures lower

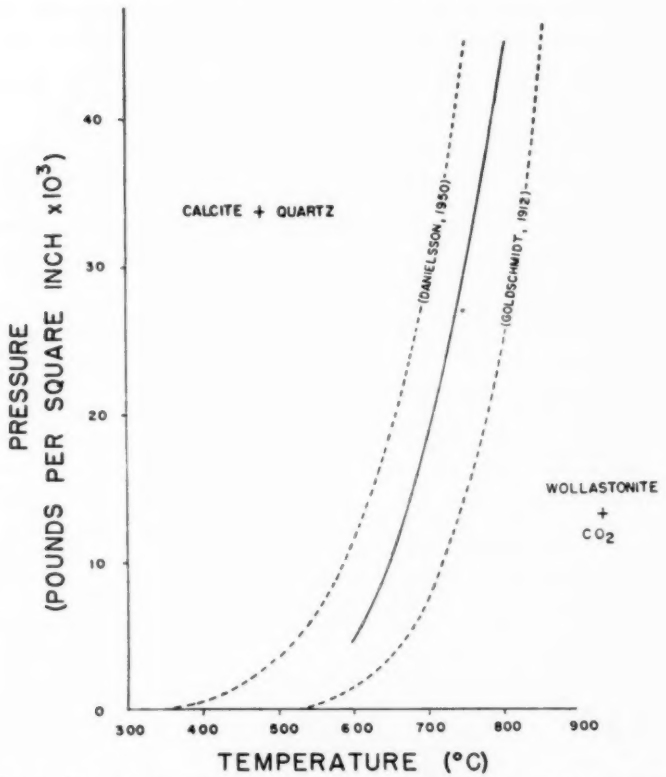

Fig. 6. The experimentally determined wollastonite P-T curve (solid line) compared to the theoretical P-T curves of Danielsson and Goldschmidt.

than those at which satisfactory equilibrium experiments can be carried out must therefore be considered.

It has been possible to estimate the approximate position of the wollastonite P-T curve at pressures below 5000 lbs./in.^{2} by a simplified mathematical calculation. From the lowest point on the P-T curve at 605°C. and 5000 lbs./in.^{2}, a value for the enthalpy, ΔH, was calculated from the Nernst approximation formula, $\log p = \frac{-\Delta H}{4.571.T} + 1.75. \log T + 3.2$ (ΔH equals approximately 23.4 K.cals/mole.). Next it was calculated how this value for ΔH would vary at several successively lower temperatures in accordance with Kirchhoff's law, the necessary heat capacity data being taken from Kelley (1949). As all the calculated points for the extrapolation lay below 580°C., the heat capacity data for low quartz was used as it was estimated that the P-T curve for the high-low quartz inversion (Yoder, 1950) will cross the wollastonite curve at a quintuple point at approximately 580°C. Using the

appropriate values for ΔH for the different chosen temperatures, the Nernst approximation formula and the van't Hoff's integrated form of the Clapeyron equation, $\ln \frac{P_2}{P_1} = \frac{\Delta H}{R}\left(\frac{T_2-T_1}{T_1T_2}\right)$ were employed to determine the pressures on the P-T curve at successively lower temperatures.

The results of extrapolating by these two equations are shown in figure 7. The difference between the two reaches a maximum of 30°C. at 300 lbs./in.^{2}. In these extrapolations several factors have been ignored which may not in fact be negligible but whose importance is certainly less at lower than at higher pressures. The departure from ideality of the CO_2 gas has been ignored, and the volume of the solid phases has not been taken into account. From Kennedy's (1954) work on the P-V-T relations in CO_2 it is possible to estimate that at 610°C. and 5000 lbs./in.^{2} the departure from ideality is about 5 percent and the change in volume during the course of

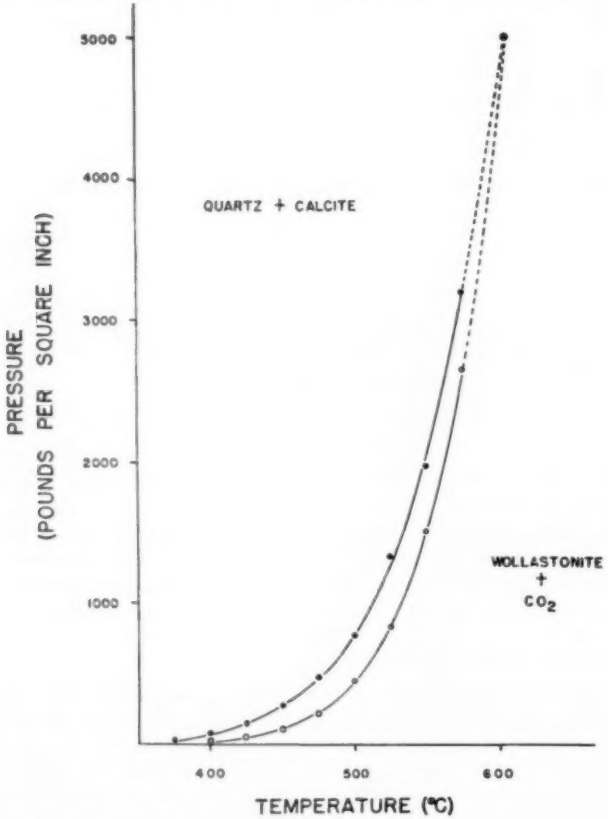

Fig. 7. Extrapolations of the experimentally determined wollastonite P-T curve by the Nernst approximation formula (o) and van't Hoff's equation (•).

the reaction is about 10 percent greater when the volume of the solids is ignored than when the volume of the solids is taken into account. Both these percentages are reduced at lower pressures, but it must be emphasized that the calculated extrapolation is only an approximation. Furthermore, it is to be expected that there will be a small discontinuity in the P-T curve at about 580°C. as a result of the α-β quartz transition.

It is clear that with such extrapolations in general the best results are obtained if the lowest point on the experimental P-T curve is determined with the greatest possible accuracy; also, the lower the temperature and pressure of this last experimentally determined point, the more valid the extrapolation will be, especially where CO_2 is involved. Clearly much time and effort is needed to determine points at low temperatures and pressures where usually reactions are slow and equilibrium is not easily attained. If, however, the extrapolations are made using equations which assume ideality of the fluid phase and which regard the volume of the solid phases as negligible compared to that of the fluid phase, then the basis of such calculations, i.e. the lowest point on the experimentally determined P-T curve, should itself involve the smallest possible departure from ideality and the greatest possible specific volume of the fluid phase.

An extrapolation of the dolomite curve might be made in a similar manner to that in which the extrapolation of the wollastonite curve was made if the necessary heat capacity data were available. However, unfortunately, it is to be expected that the enthalpy for the dissociation of dolomite varies in a more complicated way than would be covered by the straightforward application of Kirchhoff's law as in the previous case for wollastonite. This is because the amount of magnesium in the calcite of the decomposition products is itself dependent on the pressure and temperature of the decomposition (Graf and Goldsmith, 1955). However, Graf and Goldsmith have determined the dolomite curve experimentally down to one atmosphere of CO_2, and their curve combined with that determined at the higher temperatures and pressures (Harker and Tuttle, 1955) is shown in figure 8. In this figure the extrapolation of the wollastonite curve derived from the Nernst approximation formula is also shown, and it appears that the wollastonite and the dolomite curves do not cross one another.

Further evidence that these two curves do not cross can be obtained by an extrapolation of the magnesite curve. If at some pressures of CO_2 periclase is to form at lower temperatures than wollastonite, then the P-T curve for the dissociation of magnesite must also cross the wollastonite P-T curve. It is indeed possible to imagine that the dolomite curve might cross the wollastonite curve without the magnesite curve doing so, but in such a case the dolomite curve would then have to intersect the magnesite curve. Even if dolomite were unstable below the magnesite curve it could not break down to calcite + periclase + CO_2 because below the magnesite curve periclase + CO_2 do not constitute a stable assemblage. It must be concluded therefore that if periclase + CO_2 could be stable together at lower temperatures than wollastonite + CO_2, at any given pressure, then the magnesite curve would have to cross the wollastonite curve. The products of the dissociation of magnesite

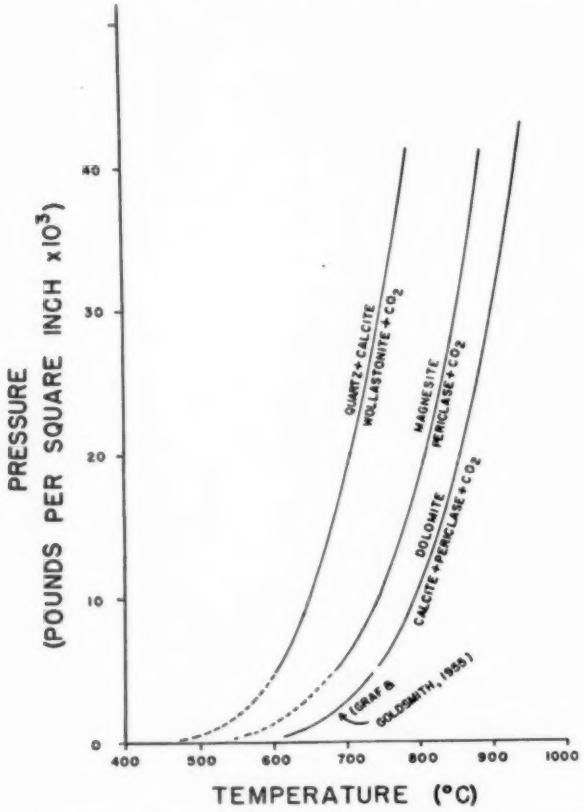

Fig. 8. P-T diagram to show the relative positions of the P_{CO_2}-T curves for the limits of stability of (a) dolomite, (b) magnesite, and (c) calcite + quartz.

are assumed to be of constant composition, so it has been possible to extrapolate the magnesite P-T curve to lower pressures and temperatures by the approximate calculation utilized for the wollastonite P-T curve. Since the publication of the P-T curve for the thermal dissociation of magnesite (Harker and Tuttle, 1955), some additional runs have been made, and it is confirmed that the P-T curve passes between 670 and 690°C. at 5000 lbs./in.^{2}. The magnesite curve has been extrapolated to lower temperatures and pressures using the Nernst approximation formula, as indicated by the dashed line in figure 8, from the point at 680°C. and 5000 lbs./in.^{2} and apparently does not cross the wollastonite curve.

It is nevertheless difficult to find conclusive petrographic evidence on the relative disposition of the wollastonite and dolomite P-T curves. If, with rising temperature, dolomite ever breaks down to periclase + calcite + CO_2

before quartz + calcite become unstable to form wollastonite + CO_2, one would expect to find periclase + calcite assemblages and quartz + calcite assemblages occurring stably over some range of temperature and pressure of CO_2. However, as the two reactions represented by the two P-T curves take place in rocks of different composition, it is unlikely that periclase, calcite, and quartz could ever be in stable equilibrium with one another in a metamorphic rock in the presence of excess CO_2 even if dolomite can break down before wollastonite is formed. Nevertheless one might expect periclase + calcite assemblages to occur in close association with quartz + calcite assemblages in rocks which varied sufficiently and appropriately in composition, such as a banded sedimentary series of siliceous limestones and dolomites or in skarns. In a valid example it would be necessary that the assemblages occur close together so that it would be fairly certain that they had developed as a result of the same P-T conditions. Also if brucite occurred it would be necessary to be sure that it had in fact developed from periclase and not in any other way. Up to the present no petrographic evidence of these two assemblages in close association has been found.

Bowen (1940) examined Harker's (1904) petrographic description of the thermally metamorphosed carbonate rocks in the vicinity of the Tertiary igneous rocks of Skye and noted that although periclase was developed from dolomite, no wollastonite was formed even about flint nodules. Subsequently, Tilley (1951) described the contact rocks in the Strath Suardal Limestone adjacent to the Beinn an Dubhaich granite, and observed (p. 623): "Wollastonite has so been noted in association with diopside in the dolomite of the old marble quarries. . . . " It appears likely therefore that wollastonite and dolomite may have been stable under the same conditions of pressure and temperature. The general lack of wollastonite about the flint nodules in the carbonate rocks surrounding the Beinn an Dubhaich granite except in the skarns is probably due to the high magnesium content of the carbonate rocks, causing the prolific growth of diopside, rather than to the continuing stability of a calcite-quartz assemblage.

In the region of the Beatrice Mine at Selibin in the Federated Malay States (Willbourn, 1926) granitic rocks have invaded strongly dolomitic limestones. Around pegmatites wollastonite has developed but no breakdown of dolomite is recorded.

These associations of wollastonite assemblages and dolomite assemblages appear to represent P-T conditions in the divariant region above the wollastonite curve but below the dolomite curve.

From the experimental evidence and the general petrographic evidence it is concluded that it is unlikely that at any given pressure of CO_2 periclase is ever stable at lower temperature than wollastonite.

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X-RAY DIFFRACTION STUDY OF INORGANIC STRUCTURAL UNITS IN FOSSIL WOOD

G. B. MITRA and J. SEN

ABSTRACT. About nine minerals have been identified by the X-ray diffraction method in a silicified wood belonging to an undetermined species of *Dadoxylon*. Of these, seven are reported for the first time as occurring in petrifaction. Low-quartz is by far the dominant mineral species present in the fossil wood. The quantitative estimation of the different minerals present in the material, now being done, is likely to indicate whether or not carnegieite and amesite and a few others are also petrifying minerals.

INTRODUCTION

The structural units of well preserved petrifactions are the extremely small grains of different species of minerals that fill up the cell cavities and variously impregnate, and in extreme cases, replace the remnants of the original cell wall. Thus the anatomical organization characteristic of a species is preserved. Sometimes the organic structure has been variously disturbed and destroyed preceding and during fossilization, as for example by unfavorably large crystals of the petrifying mineral. Probably the different species of minerals involved in the petrifaction, however small the grains may be, also preserved plant tissues differently. Thus Andrews and Mamay (1952, p. 67) found that preservation is generally poor in iron sulphides. The identification of petrifying minerals in variably preserved materials will, therefore, gradually make it possible to determine the relative value of different mineral species in the preservation of ancient plant life. Knowledge of the petrifying minerals is necessary for studying the structure of variably mineralized cell walls in fossil plants and in understanding some of the unknown events associated with the fossilization process. Some of these will de described elsewhere.

The mineral sources of petrified wood and of our coal seams may be the same since their woody mother substances might have drifted in similar lakes or rivers under similar conditions before they were deposited. In the Northern Hemisphere, where the coal balls containing the petrifactions occur in the coal seams proper, the mineral sources are more likely to be the same. The identification of minerals in petrifactions is likely therefore to offer some clues as to the assemblage of minerals present in coal. In the present work, X-ray diffraction method has been used to identify the minerals in petrifactions from the Lower Gondwana strata, where the particle size of the minerals, both in the coal and in the petrifaction, is usually so small that the grains cannot be identified by the petrological microscope.

MATERIAL

The material consists of a piece of silicified wood of *Dadoxylon* sp. collected from Mahuda in Bihar, in the Upper Permian of India.

EXPERIMENTAL PROCEDURE AND RESULTS

The untreated sample was powdered in an agate mortar and made into a thick paste with collodion dissolved in ether. A cylindrical fiber less than 0.5 mm in diameter was made, which hardened rapidly as the ether evapor-

ated. The fiber was mounted on the axis of a cylindrical camera (10 cm diameter) and was centered with the help of a goniometer head. The X-rays ($CuK\alpha = 1.54$ A.U.) from a Hadding tube running at about 60 k.v. and 8 to 10 ma. were used. The time of exposure was three hours.

TABLE 1

Results of the X-ray Diffraction Study of *Dadoxylon* sp.

Serial no.	θ	d Å	Intensity	Serial no.	θ	d Å	Intensity
1	4°58′	8.95	M.S.	22	27°57′	1.64	V.V.W.
	7°27′	5.92		23	29°20′	1.57	V.S.
2	9°10′	4.81	V.W.	24	31°8′	1.49	W
3	9°47′	4.53	M.W.	25	32°8′	1.45	V.W.
4	10°15′	4.32	S	26	33°13′	1.40	V.S.
5	11°29′	3.87	M.S.	27	34°37′	1.36	V.W.
6	11°57′	3.72	S	28	35°0′	1.34	V.W.
7	12°35′	3.53	M.S.	29	35°43′	1.32	W
8	13°2′	3.42	V.V.S.	30	36°57′	1.28	W
9	15°40′	2.85	V.W.	31	37°53′	1.25	V.W.
10	16°12′	2.75	W	32	38°58′	1.22	M.S.
11	17°23′	2.57	W	33	39°35′	1.20	M.S.
12	17°51′	2.52	M.W.	34	40°50′	1.18	W
13	18°43′	2.40	V.W.				
14	19°25′	2.32	M.S.				
15	19°52′	2.26	W				
16	20°48′	2.17	M.S.				
17	22°3′	2.05	W				
18	22°22′	2.02	W				
19	24°32′	1.85	V.S.				
20	26°14′	1.74	W				
21	26°47′	1.71	S				

V.V.S.—Very Very Strong
S.—Strong
M.S.—Medium Strong
M.W.—Medium Weak
W.—Weak
V.W.—Very Weak
V.V.W.—Very Very Weak

The minerals were identified following the method developed by Mitra (1950, p. 133-34; 1954a, p. 318-322); the spacings of the characteristic lines of different minerals in a standard chart prepared for this purpose were compared with those of the wood sample under examination.

Some of the weak lines of the less abundant constituent minerals were missing in the diffraction photograph. A rigidly consistent standard has been followed in determining which lines should be omitted. If for a certain mineral a line of particular intensity is missing from the pattern, then no other line of equal or less intensity has been admitted as belonging to this mineral. Where two or more lines overlap, the sum of the intensities of the lines of the constituent minerals has been found to agree with the intensity of the resultant line in the powder pattern of the substance to be identified. Following these rules, in spite of the complexity of the diffraction pattern, nine minerals could be identified in the *Dadoxylon* sp.

The minerals identified are low-quartz, magnetite, pyrite, carnegieite, serpentine, amesite, willemite, dickite, and brucite. From the X-ray diffraction data it is apparent that quartz forms the main bulk of the material. Carnegieite and amesite are also quite abundant, however. Magnetite, pyrite, dickite, and brucite seem to be present in small quantities. A rather large number of lines of serpentine and willemite seem to agree with the diffraction pattern of the fossil, but in the absence of quantitative data their identification cannot be considered certain. Quantitative estimation of the minerals by the X-ray diffraction method developed by Mitra (1954b, p. 337-338) is now in progress. It is difficult to determine at present how many of these mineral species are actually responsible for causing the petrifaction of the wood under investigation. Excepting quartz and pyrite, these minerals were apparently not known before in petrifactions, judging from the list prepared by St. John (1927, p. 729).

The orientation of the mineral grains in this and similar petrified materials is now being studied by the X-ray diffraction method to ascertain the nature of growth fabrics in petrified wood, and to determine whether the anisotropy in the original wood may be reproduced in the fossils.

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THE UNIT CELLS OF CALCITE

Professor D. J. Fisher has just written me about the startling similarity between parts of my article in this JOURNAL (v. 254, p. 65-70) under the above title, and the excellent discussion of the same subject by Henry, Lipson, and Wooster (1951, p. 162-167). Now that this is called to my attention I realize that I saw their book several years ago and must certainly have seen their figure 166, which my figure 1 resembles closely. I sincerely regret that I overlooked their work, and wish to cite it here not only as the source of inspiration for figure 1 but as an important reference with excellent discussions of the unit cells of calcite, and of the principles underlying, and uses of, the transformation matrices given in my tables 1 and 2. My purpose in preparing the article was to summarize for the general-geological reader certain important and well-known crystallographic results that may simplify his problems in reading recent literature on petrofabric analysis and on artificial deformation of rocks. Such a repetition and review of crystallographic specialists' results was needed, but of course I should have referred to Henry, Lipson, and Wooster when using a diagram that is so similar to their figure.

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HORACE WINCHELL

REVIEWS

Theoretical Structural Metallurgy, 2d ed.; by A. H. COTTRELL. P. viii, 251; 132 figs. New York, 1955 (St. Martin's Press, $4.50).—The appearance of the first edition in 1948 of *Theoretical Structural Metallurgy* by A. H. Cottrell was something of an event. Prior to its publication there existed a number of texts and monographs which, in their time, were definitive treatments of the field of research and engineering that is metallurgy. But, for the most part, these earlier works were concerned with a descriptive discussion of metallurgical phenomena; the theoretical formulation of the science of metals was largely left to the solid state physicist and it was neither readily accessible nor, in some cases, readily understood without a considerable background of theoretical physics. The earlier edition of this book presented for the first time a systematic and readable account of the theoretical basis of metallurgy suitable for metallurgical teaching.

Considering that only those topics are covered for which a reasonably complete theoretical basis exists, the necessity for a new edition in seven years because of the development of theoretical understanding in areas not capable of theoretical treatment in 1948 is a remarkable testimony to the rate of growth of the science of metals. It is also a measure of the problem confronting the teacher of metallurgy, both in the choice of material and in the absence of suitable texts.

The present edition is substantially rewritten, and numerous topics have been included for the first time, notably in the field of plastic deformation

and surface energy. The original outline, which was based on the fact that an understanding of metals can only be obtained through a consideration of the properties of atoms and the forces binding atoms into metallic structures, has been preserved, but a quantum mechanical treatment is used exclusively rather than the historical development originating in classical mechanics.

The first three chapters consider the structure of the atom, the forces between atoms, and the crystallographic arrangement of atoms in metallic crystals. The following three chapters are devoted to a simplified treatment of the quantum mechanics of electrons in a periodic lattice, together with applications to conductivity, ferromagnetism, and cohesion; in these chapters a very successful compromise has been effected between simplicity and sufficient precision for the purpose. The next five chapters, essentially thermodynamic in character, are concerned with thermal properties of alloys, the thermodynamic development of phase diagrams, and the existence of phases in terms of free energy and the conditions governing the balance of energy and entropy. The last four chapters consider individual topics—diffusion, order-disorder phenomena, kinetics of solid state phase transformations and, finally, plastic deformation and structure-dependent properties of crystals in terms of dislocation theory.

While all chapters contain new material and new treatments, the last chapter on dislocation theory and plastic deformation is perhaps the one topic that could not be omitted from a book carrying the present title and it probably constitutes the main driving force for the publication of this new edition, especially as Professor Cottrell is one of those most active in the development of dislocation theory. The chapter considers the geometrical and elastic properties of dislocations and outlines their application to substructures, small angle boundaries, the martensite transformation and the phenomena of the yield-point. However, this topic is covered in the space of 22 small pages, and it seems that the importance and success of dislocation theory warrants a more detailed exposition of the phenomena which it has explained so successfully.

Indeed, while one should be grateful for what is presented, many topics warrant a somewhat more extensive treatment. This could be achieved by the elimination, if necessary, of some topics like X-ray diffraction and crystallography which are too limited in treatment to serve their purpose and for which adequate texts already exist. In its present form the book requires a considerable amount of supplemental material to "get it across" to undergraduate students; first-year graduate students have matured sufficiently to read it more or less unassisted and for these it serves as an excellent introduction to the more detailed monographs and texts that are listed at the end of each chapter.

We have enough books on metallurgy written for everyone except the metallurgist. For some years to come this book will probably serve as a point of departure for subsequent texts on metallurgy and, likewise, as a pattern for courses in the fundamentals of physical metallurgy.

W. D. ROBERTSON

Semaine d'Etude sur le Problème des Microseismes. P. ix, 417; 172 figs. Pontifical Academy of Sciences, 1952.—The problem of the origin of microseisms has been a subject of scientific controversy for a great many years, and as a result a multitude of divergent opinions have been advanced in an effort to resolve the phenomenon. Because of its diverse aspects and the extensive but inconclusive study devoted to it, this problem became an apt subject for discussion by the Pontifical Academy of Sciences. The results of these discussions have been collected and edited under the supervision of the Academy and published as a paper-bound volume entitled *Semaine d'Etude sur le Problème des Microseismes.*

This volume consists of 19 papers on the origin of microseisms, 9 in English, 4 in French and 2 each in German, Spanish and Italian. The papers are accompanied by graphs, illustrations, tables and seismograms, and in some cases a bibliography is included which in itself is a valuable guide to further research. The relative merits of each paper are discussed, in French, by those attending the meeting.

The statement of the problem to be discussed is presented by Professor Francesco Vercelli, Director of the Talassografico Institute in Trieste, Director of the Geophysical Observatory in Trieste, and President of the Italian Geophysical Society. This preface summarizes the history of thought on microseisms down through the years.

A random perusal of the volume discovers such interesting topics as "The Period of Group Microseisms" by Rev. E. Gherzi, S.J., Director of the Meteorological and Seismic Observatory of Zi-Ka-Wei (China); "A Study of Small Microseisms of Periods 3/10 to 5/10 of a Second" by Rev. J. B. Macelwane, S.J., Director of the Department of Geophysics, St. Louis University; "Microseisms of High Frequency" by Professor R. Stoneley, President of the International Association of Seismology; "The Microseismic Time Lag Problem" by Professor J. P. Rothe, Director of the Institute of Physics of the World and Secretary General of the International Seismological Society; "On the Microseismic Movement Recorded in Greenland and its Relation to Atmospheric Disturbances" by Professor I. Lehmann, Director of the Seismological Section of the Geodetic Institute, Copenhagen; "Review Over Investigations of Microseisms in Scandinavia" by Professor K. M. Bath, Professor at the Meteorological Institute of Uppsala.

The lack of a table of contents renders the use of the volume awkward; however, the value of this publication is enhanced by a summary of the conclusions arrived at through the presentation of the papers.

Although much speculation on the origin of microseisms still exists, this collection of works gives the research worker, student or interested reader in the field of microseismology a handy reference volume and a compact, concise and authoritative guide to the study of microseisms.

WAYNE J. COSTLEY

Geology of Olympic National Park; by WILBERT R. DANNER. P. 68; 50 figs. Seattle, 1955 (University of Washington Press, $1.25).—Much of the Olympic National Park still remains virtually unexplored, and only the out-

lines of its geology are known. It is unique among Park areas in that its terrain ranges from rain forest to glacier-clad peaks exceeding 7500 ft. in altitude. The thoughtful tourist will gain great benefit from this clear exposition, pleasantly written in nontechnical language, of the morphology and geologic history of this region of complex rocks. The pamphlet is illustrated with a sketch map, line drawings, and many photographs, most of which are excellent. It is highly recommended reading for anyone who plans a visit to the Park.

RICHARD FOSTER FLINT

Géologie des barrages et des aménagements hydrauliques; by M. GIGNOUX and R. BARBIER. P. 344; 176 figs., 28 pls. Paris, 1955 (Masson et Cie., 3500 francs).—This textbook on the geology of dams and related works is an outgrowth of the authors' course in applied geology given at the Ecole Nationale Supérieure d'Hydraulique in Grenoble. We are told in the Introduction that it was written primarily for engineering students, although in the reviewer's opinion the book lends itself equally well to the needs and capabilities of the geology student. Written for students with a technical training not unlike that found in most American universities, it is not a brief introduction into the mysteries of either engineering or geology but rather an extended tour through the complexities of dam-site geology.

The presentation is that of case histories, which are, as the following chapter headings indicate, arranged to elucidate and illustrate general principles: the topographic factor, overburden, landslides and related earth movements, problems posed by storage dams, tunnels, examples of subsurface storage systems, and drilling and grouting. To the reviewer's knowledge, the only case history of dams in English at all comparable in scope is Technical Report 22, Tennessee Valley Authority, "Geology and foundation treatment; Tennessee Valley Authority projects." The case histories of Gignoux and Barbier's book are drawn almost exclusively from southeastern France and French North Africa. Nevertheless, because of a most carefully planned and thoroughly executed text, a vast array of geologic problems and their solutions is presented. The complex geology and spectacular topography of the French Alps have been responsible for a very diverse series of ingeniously designed dams. Not only are the geologic factors entering into the design and construction of these dams explained but the negative examples of rejected dam sites are also given full weight—as they should be, but rarely are, in pedagogic treatment of this subject.

An unfortunate shortcoming of the book, from the American standpoint, is the lack of stress given earth-fill dams and construction on and with soils. This, the authors freely admit (p. 112), is the result of the almost entire absence of large earth-fill dams in France. The book is therefore largely concerned with concrete and masonry dams, although several interesting earth- and rock-fill structures in North Africa are described. More difficult to justify, however, is the cursory recognition given to the complexity and critical nature of soils, both as foundation and construction material. Many engineers and engineering geologists alike will question the soundness of the statement, in briefly alluding to the soil foundations of earth- and rock-fill dams (p. 104):

"Problems of compressibility and strength are not, in general, very important . . . . ", or for that matter the wisdom of minimizing the importance of soil mechanics to the student, as on page 150 where it is said categorically that existing slopes provide a better guide than soil mechanics for the design of slopes in *heterogeneous* soils. The student probably will not know the geologic limits to soil mechanics' usefulness and therefore should not be led to dismiss this technique without at least the concurrence of a soil engineer.

Physically, the book is of excellent quality: well bound and well printed. It is profusely illustrated with 176 line drawings of fine clarity and 28 exceptional photographs, many of which are double-page panoramas of rare beauty. Captions are lengthy and explicit and are in both English and French. The table of contents, list of illustrations, and other normally prefatory material are in the back of the book. The book is recommended as a text and as a guide in setting up similar courses in engineering geology in the United States.

CLIFFORD A. KAYE

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